

California Environmental Protection Agency



SOP MLD 024

**STANDARD OPERATING PROCEDURE FOR THE DETERMINATION
OF TOTAL NON-METHANE ORGANIC COMPOUNDS IN AMBIENT AIR
USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME
IONIZATION DETECTION (PDFID)**

Engineering and Laboratory Branch
Monitoring and Laboratory Division

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S.O.P MLD 024

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TOTAL NON-METHANE ORGANIC COMPOUNDS (NMOC) IN AMBIENT AIR BY USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME IONIZATION DETECTION

1. SCOPE

This document describes the method for the analysis of total non-methane organic compounds (NMOC) in ambient air. Developed from USEPA 600/4-85/063, this method involves the cryogenic preconcentration of an ambient air sample with subsequent determination of total NMOC concentration represented as a single peak by direct flame ionization detection. The method provides a rapid analysis of ambient samples (a quick survey of total NMOC levels from various sites) and permits a cross-check with results from the speciated NMOC analyses by flame ionization detection (FID).

2. SUMMARY OF METHOD

Ambient air is sampled over a three-hour period and collected in a SUMMA passivated stainless steel canister using XonTech 910A sampler. All the operational procedures and sampling conditions are documented. A record of this information is sent back to the Engineering and Laboratory Branch (ELB) organics laboratory along with the sample for immediate analysis. Upon arrival into the laboratory, the canister sample must be equilibrated to room temperature for at least one hour before analysis. The integrity of the canister pressure is validated by using a calibrated gauge. All information from the canister is documented in the login protocol, and the canister is analyzed according to the chain of custody within the laboratory.

A 300 cc ambient air sample is introduced into the system from the pressurized canister through 1/16" stainless steel tubing with the aid of a mass flow controller and a vacuum system. For low sample volumes, a fixed volume loop of 10.0 cc can also be used. The digital flow meter readout that is attached to the gas chromatograph (GC) provides a visual indication of the proper sample flow during sampling. Automatic sampling of up to 16 sample containers can be accompanied with a multi-position automated sampler which is controlled by the GC or personal computer (PC with Star Workstation software). The sample passes through a Nafion dryer to remove moisture (H₂O vapor) from gas streams

and is trapped within nickel tubing ((~ 500 μ L) filled with silanized glass beads (60/80) mesh at -168.8°C . The desired NMOC components are immobilized (solidified), while oxygen (O_2), carbon monoxide (CO), and methane (CH_4) pass through the vent. The injector is purged with N_2 , followed by sample heating and injection. The trap is isolated and heated to 190°C at the rate of $300^{\circ}\text{C}/\text{min.}$ to completely volatilize the trapped hydrocarbons. The gaseous sample is purged off the trap with nitrogen (N_2) and injected directly into the flame ionization detector (FID). An additional 1.80 minute hold at 190°C of the isolated trap, allows sample to be completely volatilized (especially the higher boiling components) before the sample is purged to the detector by N_2 . Since the analysis does not utilize a column, all NMOC compounds are represented as a single peak and are subsequently quantified as total NMOC.

3. INTERFERENCES AND LIMITATIONS

- 3.1** Excess moisture, especially with large sample volumes, not extracted by an inline Nafion Dryer and trapped with the sample, can interfere with the FID signal, producing elevated baseline and tailing. Correction by data system integration can offset most of these effects. Also, high levels of water and carbon dioxide can trigger trap blockage, causing incomplete sample loading and must be avoided. Blockage can be detected by elevated pressure readings on purge gases during trap flushings. The problem can be minimized by injecting smaller sample volumes or by using small volume (*i.e.* 10cc) fixed loop sampling.
- 3.2** A FID connected to a cryotrap may periodically display flame blowout as a result of pressure variations from rapid cooling/heating of the trap. A one-foot section of narrow bore (0.1 mm ID) fused silica is placed just before the detector to serve as a buffer from these pressure surges.
- 3.3** CO_2 , CO , N_2 and O_2 do not respond to FID, however O_2 can cause disruption in flame characteristics and baseline perturbations at high sensitivity range settings. Using larger sample volumes with lower sensitivity ranges for analysis is recommended.
- 3.4** Insufficient cooling provided for the cryotrap may cause inefficient trapping of organic compounds, especially C_2 hydrocarbons and propane. Check to ensure that the trapping temperature is maintained at -168.8°C during the thermal stabilization period. If the trap temperature deviates well below the set temperature, then CH_4 and O_2 are trapped, causing baseline perturbations, and trap plugging by CO_2 , which interfere with detection.
- 3.5** Improper use of mass flow controller (MFC), especially when introducing measured sample volume into the system, will produce significant errors in the final results. Periodically observe the MFC's actual sampling rate from the digital flow meter readout to ensure that there is good agreement, and that these settings are at the calibrated range for the instrument. Also, air streams with high

level of CO₂ (>50%) can also introduce significant lower volume errors and should not be used with MFC sampling. However, fixed loop sampling can be used for high levels of CO₂, since the sampling is independent of bulk gas composition and produces best precision with low volume sampling.

- 3.6 Other typical problems encountered can be a dirty FID jet, a plugged jet and improper flame gas flows. Optimization, involving setting the carrier, hydrogen, and makeup gases, should be performed whenever peak signature has changed (peak broadening, multiple peaks, significant changes in retention times). It is also important that the instrument maintains consistent settings. In addition, preventive maintenance should be performed at least once a year.

4. APPARATUS

- 4.1 A Varian Model 3600CX GC equipped with sampling hardware (available 16 or 32-port multiposition automated sampler), gas pneumatics with High Performance Valves (Valco Instruments), high temperature version (Series T), vacuum, continuous self regenerating dryer (Nafion, Perma Pure Inc., or equivalent) for removal of water vapor from gaseous streams, concentrator trap with glass beads absorbent (60/80 mesh), and a single FID. The principles of gas chromatography and a brief overview of FID is documented in Appendix II.
- 4.2 The 3600CX GC is equipped with a digital flow controller and a pressure regulator (set in parallel) to minimize flow upsets during valve switching. The digital flow controller and the pressure regulator are installed in the heated pneumatics compartment which is heated isothermally to 45°C. A digital flow controller (Sierra Instruments, Inc., 0-100 sccm/min.) is calibrated to deliver a flow from 0-100 sccm/min. \pm 3% for nitrogen (N₂) with an inlet pressure of 80 psi (with a minimum pressure drop of 10 psi, to perform to specification).

Note: *Pressure gauges or electronic pressure readouts (EPRs), give a visual display of column pressure and are used for carrier gas monitoring and problem diagnostics (displayed on the pneumatics panel in front of the GC).*

- 4.3 Teflon tubing (1/8" OD x 1/16" ID, 0.030 wall) and brass fittings for autosampler-to-canister connections.
- 4.4 Carrier Gas Filter (Varian P/N 03-949770-02 or Supelco P/N 2-2445M, or equivalent).
- 4.5 A Varian GC Star Workstation, IBM compatible, PC based, for GC system control, automation, and method editing. Appendix III.
- 4.6 A Perkin-Elmer Turbochrom data system, version 4.1 <2F12>, IBM PC based, for data collection, storage, and quantitation. Appendix I.

- 4.7 A Perkin-Elmer Nelson 900 Series Analog/Digital Converter (model 970).
- 4.8 Stainless steel canisters with interior surfaces treated by the SUMMA passivation process, used for sample and standard storage.

5. REAGENTS

- 5.1 System blank such as head space liquid nitrogen is used for the instrument check. If stored in canister, system blank (e.g., zero air, ultrapure air, or ultrapure N₂) is treated and introduced into the system in the same manner as a sample. It is analyzed before each set of sample analyses.
- 5.2 A certified NIST traceable hydrocarbon standard mix containing propane standard in air of 0.250 ± 0.003 mmol/mol (CLM-09772) is used for daily one point calibration of the instrument. Since all concentrations are reported in units of parts per billion carbon (ppb C) to correct for variations in detector response to various hydrocarbons on a volume to volume basis, the propane standard concentration is expressed as 750 ± 9 ppb C. This mix is also used for multipoint analysis to establish linear dynamic range of the detector, as well as limit of detection (LOD) of the instrument. The standard should be slightly higher in concentration with respect to the typical sample and be within the linear dynamic range of the instrument.
- 5.3 A control sample (CC113544) from Scott-Marrin, Inc. containing ethane in nitrogen at 1500 ppb C, which is within the upper linear range of the multipoint calibration, is used to measure the reliability of the calibration of the GC system and to evaluate the overall measurement process. A multicomponent traceable hydrocarbon mix (ALM009023), having nominal value of 244 ppb C is used as a secondary control sample to simulate low ambient air concentration and to measure the reliability of the calibration at the lower end of the linear curve.
- 5.4 Nitrogen, Grade 5 or ultrapure ($\geq 99.9999\%$), as a carrier gas, foreflushing gas, and as a counter-flow drying gas in the Nafion dryer. Note that the nitrogen (foreflushing gas) sweeping through the trap to the MFC is cryogenically cleansed prior to use, with any trapped material vented to atmosphere after each sample cycle.
- 5.5 Helium, Grade 5 or lower purity, as a valve actuator gas.
- 5.6 Liquid Nitrogen for cryogenic preconcentration and sub-ambient GC analysis. Head space nitrogen is also used for system blank analysis.
- 5.7 Hydrogen, Grade 5 or ultrapure ($\geq 99.9999\%$), as a detector fuel gas.
- 5.8 Zero Air, for flame ionization detector oxidant.

- 5.9 HPLC grade water (150 mL H₂O in 6L canister), for humidification of the standard hydrocarbon mix as well as for other hydrocarbon gaseous mixtures prepared in the SUMMA passivated canisters to simulate the humidified ambient air sample. The addition of water minimizes any possible active surface sites within the canister.
- 5.10 Isopropyl alcohol/water (1:1), for leak detection (external application).

6. INSTRUMENT CONFIGURATION AND PARAMETERS:

- 6.1 The analytical system and automation configurations are shown in Figures 1, 2, and 3. The valving diagrams depict the system configuration for normal operation (valve 3C (-) *off*), the use of MFC for sample introduction (valve M-A (+) *on*, valve M-B (+) *on*), and the use of 8134 SSV relay for ports 1-16. Valve 3C is manually configured to -3 (*off* – normal operation)/+3 (*on*-canister test) by a toggle switch located on the left side panel of the GC. Valves M-A and M-B are also manually configured to *off* position (fixed loop sampling) or *on* position (MFC sampling) by a separate toggle switch also located on the left side panel of the GC. Selection for streams 1-16 or streams 17-32 depends on the valve 2A setting, with -2A (*off*) streams 1-16 are selected and with +2A (*on*) streams 17-32 are selected.¹ Valve 1A (*delayed*) is set to activate at a defined time period, after the primary events occur. Valve 1A (*delayed*) is set to activate 1 second after event 1(+1) occurs, by configuring the valve actuation for 00001 in Mode D (Sec). Valve 4A (isolation of the trap) is controlled by event ± 2 and valve 4B (sample directed to trap or deleted) is controlled by event ± 4 . These settings are to be considered as “system defaults” for total PDFID analysis, using method pdfid74.mth (Star Workstation).
- 6.2 There are six separate temperature zones that are defined under Module Address 17: **GC Injector A** (Valve 1A, M-A, 3B), **GC Injector B** (Cryotrap), **GC Auxiliary** (Valve B, 4B, 4A), **GC Column** (multi-position automated sampler – 2 x 16 ports 8134SSV, Valve 3A, 2, 3C), **GC Detector Heater A** (FID), and **GC Detector Heater B** (*not configured*). The interconversion of actual trap temperature (T_{act}) and injection setting (T_{set}) in Star Workstation are provided in Figure 4. **Note:** the temperature setting for the injector B (trap) temperatures does not correspond to the true temperature of the injector.

6.2.1 **GC Injector A:** Valve 1A, M-A, 3B

Should be set with high enough temperature to ensure no sample condensation (max. temp. $\leq 300^{\circ}\text{C}$).

Injector Type: Isothermal
Injector Heater: On
Initial Temperature: 150°C

¹ The Event (± 2) is no longer available for stream selection because the event (± 2) is currently used to activate valve 4A.

Coolant to Injector: On
Coolant Timeout: 10.00 minutes

6.2.2 GC Injector B: Cryotrap

Injector Type: Temp. Programmable
Injector Heater: On
Initial Temperature: -74°C (Actual Temp. -168.8°C)
Hold Time: 0.10 minute

Program:

Final Temperature: 225°C (Actual temp. 190°C)
Rate: 300°C/min
Hold Time: 1.80 minutes
Injector Program End Time = 2.89 minutes

The concentrator trap is optimized for trap volume of ≤ 500 mL for efficient transfer to the FID, and provides rapid heat/cool cycle with minimum temperature overshoots/undershoots at set points. Typical temperature profile of concentrator trap ramping is shown in Figure 5.

6.2.3 GC Auxiliary: Valve B, 4A, 4B

Should be set with high enough temperature to ensure no sample condensation (max. temp. $\leq 300^\circ\text{C}$).

Auxiliary Type: Isothermal
Auxiliary Heater: On
Description: Valving
Initial Temperature: 150°C

6.2.4 GC Column: multiposition automated sampler – 2 X 16 ports 8134SSV, Valve 3A, 2, 3C

No column chromatography is performed or installed. The temperature parameter is high enough to ensure no sample condensation.

Column oven: On
Initial Temperature: 150°C
Hold Time: 3.00 minutes
Thermal Stabilization: 0.50 minute
Coolant to column: Off
GC Column Program End Time: 3.00 minutes

6.2.5

GC Detectors:

Heater A:

Heater: On
Temperature: 200°C
Detector A Type: FID (On)
Time Program: No

Heater B:

Heater: Off
Temperature: 50°C
Detector B Type: Not Used (Off)
Time Program: No

Initial Conditions:

Attenuation: 8*
Range: 11
A/Z: Yes

*Note: The attenuation value in the GC detectors window changes the output signal to the Stripchart recorder. We are currently not using the Stripchart recorder and therefore the attenuation setting is not applicable in our method.

6.2.6

Autosampler:

Autosampler Type: 8134 SSV

6.2.7

3600 GC Stripchart:

Stripchart: Off
Time Program: No

6.3 Sample Volume Injection

Sample volume of 300cc is determined from 6.00 minutes of trapping time at a sample trapping rate of 50 cc/minute. The sample volume for the FID injection is fully automated by the use of 8134 SSV Relay Time Program which is part of the Varian GC Star Workstation software. The location of valves for Varian 3600CX GC analytical system as well as the layout for the pneumatic controls are shown in Figure 1. Table 1 lists the relays, and their corresponding degree of rotation employed in this system.

6.4 3600 GC Running Parameters:

Please notice that the GC Oven Parameters are listed in Section 6.2.4.

6.4.1 GC Relays Time Program: Relay Time Program: Use

	<u>Time(min.)</u>	<u>Relay #</u>			
<i>Start oven temp. program</i>	<i>0.00</i>	-	-	-	-
<i>Isolation of the trap/heat trap</i>	<i>0.01</i>	-	+2	-	-
<i>Injecting sample onto detector</i>	<i>1.00</i>	-	+2	-	+4
<i>Injecting sample onto detector</i>	<i>2.00</i>	-	-	-	+4

[X] *Return Relays to Initial Conditions at Run End*

6.4.2 GC Column Parameters

No column is used for this analysis. The following parameters were edited in order for the instrument to calculate linear velocity and other set conditions:

<i>Col. A Installed:</i>	<i>Yes</i>
<i>Length:</i>	<i>0.00 meter</i>
<i>Diameter:</i>	<i>0.00 micron</i>
<i>Carrier Gas:</i>	<i>Nitrogen</i>
<i>Col. B Installed:</i>	<i>Yes</i>
<i>Length:</i>	<i>0.30 meter</i>
<i>Diameter:</i>	<i>100 microns</i>
<i>Carrier Gas:</i>	<i>Nitrogen</i>

6.4.3 GC Detector Settings

<i>Detector A Type:</i>	<i>FID</i>
<i>Detector B Type:</i>	<i>Not Used</i>
<i>Detector Temp of A:</i>	<i>200°C</i>
<i>Detector Temp of B:</i>	<i>50°C</i>
<i>Detector Range A:</i>	<i>11</i>
<i>Autozero setting on GC:</i>	<i>On</i>

6.4.4 Gas Flow Settings

<i>N₂ – Carrier Gas:</i>	<i>20.10 cc/min (80 psi required pres.)</i>
<i>He – Valve Actuator*:</i>	<i>65 psi suggested pressure</i>
<i>N₂ - Nafion, Purge**:</i>	<i>50 psi</i>
<i>H₂ – Fuel Gas:</i>	<i>30.5 cc/min (40 psi)</i>

Air – Oxidant: 300 cc/min (70 psi) – House Zero Air

Note: *A separate supply gas tank is recommended for valve actuators to minimize spikes on the FID from pressure pulses when valves are turned.

** N₂ is also used for Nafion dryer counter flow dry gas, set at 150 cc/min.

7. TOTAL PDFID ANALYSIS PROCEDURE

7.1 Sample pre-injection period (Figures 2A through 2E)

7.1.1 Canister samples are connected to the Autosampler using appropriate tubing and fittings. After assurances of leak-free connections, the valves of the sample containers can be opened.

7.1.2 GC 3600CX system configuration and GC operational editing functions (sample file list, sequence list, and method building) are done on Star 3600 Workstation. See Appendix III.

7.1.3 PE Nelson 2700 data system (Turbochrom Ver. 4.1 <2F12>) is set up for data acquisition, storage, and integration. See Appendix I.

7.1.4 The sampling flow rate is regulated by a digital flow meter, Sierra Instruments Inc., which is mounted downstream of the sampling point to eliminate any contamination and to reduce dead volume in lines from sample trap. The sample volume is:

Volume = Trapping Time x Flow Rate

I.e., Volume = 6.00 min. x 50.0 sccm/min. = 300 sccm

7.1.5 The pre-injection system configuration for normal operation (Valve 3C off) and for MFC sampling (Valve M-A and Valve M-B on) is shown in Figure 2A. Standard, control and ambient air samples are introduced to the GC from automated preconcentration system by means of relay time program set in Star Workstation, edited in the Sample List file (pdfid16.smp). Time, relay, and events are set as follows:

<u>Time</u>	<u>Event</u>	<u>Valves</u>
0.00 min	-1-2-3-4	All valves are off (-). The sample flow dead-ends (port 6, Valve 1A, <i>delayed</i>), and allows N ₂ purge gas to flow through the MFC and flow meter. N ₂ gas is also directed through several valves (3A, 3B, M-B, 4A, 4B, injector B-trap) primarily

for sweeping and conditioning the system.

0.01 min	+1-2-3-4	Valve 1A, <i>delayed</i> , is on (+1), allowing sample to flow through the MFC, thus purging the lines with new sample.
1.00 min	+1-2+3-4	Valve 1A and valve 3B are activated (+1 and +3), and valve 4A and valve 4B are off (-2 and -4). The sample flow is directed through the trap. Sample loading is initiated at this time.
7.00 min	-1-2+3-4	Valve 3B is on (+3), and valve 1A is off (-1). The sample flow dead-ends, allowing N ₂ to purge the interconnecting lines of the sample and gases not trapped e.g., O ₂ , CO ₂ , CO, CH ₄ . <u>Note: By controlling the time events between activating valve 3 (+3) and turning off valve 1 (-1), the effective sample loading can be varied.</u>
7.20 min	-1-2-3-4	Valve 3B is deactivated (-3). All valves are off (-). This ends the pre-injection time events. <u>Note: This time event is only a transition step, valve 4A is activated in 0.01 minute to isolate the trap during temperature ramping stage.</u>

7.2 Sample injection/post-injection period (Figures 3A through 3C)

7.2.1 Time events for injection, specified in FC Relays Time Program, is accessed through Method Editor (pdfid74.mth) in Star Workstation.

<u>Time</u>	<u>Event</u>	<u>Valves</u>
0.01 min	-1 +2 -3 -4	Valve 4A is on (+2). The trap is isolated, heated to 225°C (<i>actual temp.</i> 190°C), and held for 1.8 min. at that temperature.
1.00 min	-1 +2 -3 +4	After 1.00 min., Valve 4B, turns on (+4), redirecting the N ₂ purge gas flow to flush the heated sample onto the FID.

2.00 min -1 -2 -3 +4

The trap is in series, the sample is purged by N₂ to the FID. Valve 4B is on (+4) whereas valve 4A is deactivated (-2).

8. ANALYSIS

In general, the sequence of analysis for Engineering Laboratory Branch methodology, including the requirements of quality control, is as follows:

1. System blank
2. Calibration
3. Control sample
4. Ambient samples
5. Sequence duplicate/replicate

- 8.1** A system blank, consisting of either ultrapure zero air, headspace liquid nitrogen, or ultrapure N₂ gas, is analyzed prior to calibration to detect system contamination. System blanks must be less than the published LOD (30.0 ppb C) before proceeding to the next step.
- 8.2** A daily system calibration is performed with a certified NIST9772, traceable primary gas standard of propane (Figure 6). The standard is prepared in a humidified (injection of 150 microliters of HPLC grade water under vacuum) SUMMA™ passivated canister that is analyzed after a system blank and before any ambient samples. The NIST propane standard is used to calibrate the instrument for all non-methane organic compounds. A single point calibration is established for each sequence using a single analysis of this external standard at 300 sccm (mL) volume. There is no “averaging” of the daily response factors. The FID detector response, in area counts, is directly related to the known concentration of the propane and is used to calibrate the instrument each time it is used. After the analysis of the standard run, the response factor (Rf) is calculated as follows:

$$\text{Rf} = (\text{Std.Conc.}) / \text{Std. Area Count}$$

i.e., **Propane** = (750 ± 9 ppb C) / Area Count

Note: The concentrations of propane in the NIST9772 standard is listed as ± 3.0 nmole/mole or ± 9ppb C. This uncertainty is due to imprecision in the preparation and analysis of the NIST standard by the EPA.

- 8.3** Control samples, CC113544, Scott-Marrin, Inc. containing ethane at 1500 ppb C (Control A), and ALM009023, a secondary multicomponent control sample having a nominal value of 244 ppb C (Control B), are analyzed before any ambient analysis and after the calibrating standard in order to evaluate the measurement process (Table 5 and Figure 7). Both control samples are prepared

in a separate humidified (injection of 150 microliters of HPLC grade water under vacuum) SUMMA™ passivated canister. The results of these control samples must fall within the control limits as defined in the MLD Laboratory Quality Control Manual (1997). Each control sample result is plotted real time on a control chart and is used on a daily basis to establish that the method is in statistical control.

- 8.4 Ambient samples are introduced and analyzed under the same conditions as the calibration standard and control samples. The resultant peak is quantified relative to the certified value of propane in the NIST standard.
- 8.5 Duplicate analyses (analysis of the same sample by the same instrument) are performed on at least 10% of the ambient samples analyzed. Data for concentrations in excess of the limit of detection (\geq LOD) are recorded. The percent difference of the duplicate analyses are recorded, and values that are \geq 5X LOD and exceed the maximum allowable percent difference are included in the Quality Control report.

9. QUALITY CONTROL CRITERIA AND CONTROL ACTIONS

- 9.1 **System blanks:** System blanks are run each time before any other GC analysis and under the same running conditions as the ambient samples. A system blank run consisting of either humidified Ultra-pure zero-air, or Grade 5 N₂ is analyzed prior to calibration to check for any system contamination (background). System blank must also be run after any sample that exceeds the linear range of the detection, to eliminate any possible carry-over and bias the next analysis in sequence. The system blank must not exceed the published LOD of 30.0 ppb C. If the LOD is exceeded, the following corrective actions are to be taken:

1. Repeat analysis.
2. Check system for leaks: Most contamination that is observed in the system blank is due to leaks, especially when the gases that serve the GC instrument have been changed. Look for obvious source of contamination especially the items that have been changed recently.
3. Clean system with wet air: Purging out the GC system with several runs of humidified air to reduce and to eliminate any source of contamination in order to meet the acceptable criteria for system blank.
4. Bake-out sample trap/system: Run the GC system at elevated temperature zones.

For any blank that exceeds 30.0 ppb C for total PDFID all the sample analyses associated with that blank are invalidated (preferably re-run at later date) and the

cause investigated and documented. The Supervisor should approve any action criteria associated with the results.

- 9.2 Daily calibration:** Prior to the analysis of samples but after the system blank, single point calibration (daily calibration) is performed. The NIST standard (CLM-09772) offers propane as a certified externally traceable primary standard for calibrating total PDFID GC instrument. The acceptance criterion for daily calibration is that the Rf value must be within ± 10 relative percent difference (RPD) of calibration curve average Rf. Attention must be given to changes in Rf values that may indicate instrument, standard gas mix, or detector sensitivity changes. The corrective action if the above criterion is not met is:

Repeat daily calibration analysis.

Check FIDs for leaks and gas flows: Detector sensitivity changes are mostly contributed to leaks in the detector and changes in gas flows. Make sure that the gas cylinder pressure requirements are met and that the gas flow settings have not been altered. If all the settings are correct, but the flow requirements are not met, check for the leak source and correct the problem. Document the corrective action taken, and repeat the daily calibration analysis.

Prepare new calibration standard sample and repeat the analysis:
Prepare a new NIST standard sample (humidified with $150\mu\text{L H}_2\text{O}$) and re-run the daily calibration.

Repeat multi-point analysis: If all the corrective actions listed above do not produce the desired result, then verify the linear dynamic range of the FID detectors, by preparing and running new calibration standards. Verify that the expected precision, accuracy, and LOD are also not compromised. The calculated precision, accuracy and the LOD must be equal to or better than the established criteria prior to the PAMS season.

- 9.3 Daily control samples:** Control samples (CC113544 and ALM009023) are analyzed after the calibrating standard and before any ambient air samples. The control results are evaluated and plotted on control charts on a daily basis. Control limit levels for each control sample are established based on calculated standard deviation (std) of at least 20 measurements of the control sample analyzed during the pre-season period. The limits are set as follows:

UCL (Upper Control Limit)	=	+3*std of Mean Value
UWL (Upper Warning Limit)	=	+2*std of Mean Value
Mean or Assayed Value	=	
LWL (Lower Warning Limit)	=	-2*std of Mean Value
LCL (Lower Control Limit)	=	-3*std of Mean Value

If the analysis of the control sample yields a result that falls outside the Control Limits (UCL/LCL), the control sample is reanalyzed. If the second results are also outside of the Control Limits, the analysis is discontinued, the Supervisor notified, and the cause of the problem investigated. All data during the period of analysis is invalidated.

- 9.4 Duplicate analysis:** Replicate analyses are performed daily (analysis of the same sample by the same instrument) and are performed on at least 10% of the total ambient samples analyzed. The relative percent differences (RPDs) of duplicate results are recorded for all samples. The maximum allowable percent difference (MAPD) for any sample with concentration equal to or greater than 150.0 ppb C should not be greater than 25%. If any duplicate sample analysis fails to meet this criterion, all data is invalidated for that sequence.

10. METHOD SENSITIVITY, PRECISION, AND ACCURACY

- 10.1** Multipoint analysis must be performed prior to the start of the NMOC season to verify the linear dynamic range of the FID detector response to various analyte concentrations. Hydrocarbon concentrations in ambient air can vary over a wide range, from very low ppb C to ppm C (parts per million). A strong positive correlation over the expected operating range ensures accurate results at other concentration levels. FID usually exhibit linearity over a 10^7 range (range set is 10^{-12} amps/millivolts at 50-microsecond time constant. Multipoint analysis is performed by changing the sampling time while maintaining a constant sampling rate in order to vary the volume and therefore the effective sample concentration of the standard analyzed. By performing triplicate analyses of at least four simulated concentration levels, with a correlation coefficient (r) of 0.98 or better, the dynamic linear range for VOCs is defined. If the concentration of an ambient sample exceeds the defined linear range the sample must be diluted (so that the diluted sample has a detector response within the defined linear range), reanalyzed, and the concentration recalculated for that particular sample.
- 10.2** As defined in the Laboratory Quality Control Manual, Revision 2.3 (1997) the Limit of Detection (LOD) is the Method Detection Limit (MDL), which is the minimum concentration of a substance that can be measured and reported with 99% confidence. The MDL is given in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as the product of the standard deviation (std) of at least seven replicate measurements of the propane standard at a concentration less than 150 ppb C and the Student t value of 3.14 for 99% confidence for seven values. See Table 4.

$$\text{LOD} = [\text{std}_{n=7}] * 3.14$$

Multipoint calibration and LOD calculation must be performed under each of the following conditions:

- a.) prior to every NMOC season and when system maintenance is performed
- b.) when minor modifications are done that may change the expected precision accuracy, and/or LOD of the measurement
- c.) when a major modification is performed that may change the analytical equipment configuration, operating conditions, change in matrix or reagents that may change the precision, accuracy, and LOD calculation.

10.3 A duplicate/replicate analysis is the analysis of the same sample twice in one sequence. Duplicate samples are chosen at random, and should account for at least 10% of the total ambient samples analyzed. The analysis of duplicate/replicate samples is a measure of the precision of the instrument. To make a comparison of two values, Percent Difference (%D) is a more meaningful statistic than RSD. The duplicate/replicate pairs are evaluated based on the following formula:

$$\%D = [y - x / y + x] * 200$$

Where %D is the percent difference, the x and y represents the corresponding concentrations of a sample for original and duplicate analyses.

10.4 The QA section provides the laboratory with performance audits (reference standards submitted in canisters as “blind” audits) to assess the accuracy of the data generated by the instrumentation. A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measure value divided by the audit value, and is expressed as a percentage, as illustrated below:

$$\% \text{Audit Accuracy} = [(\text{Audit Value} - \text{Measured Value}) / \text{Audit Value}] * 100$$

The reference value for an accuracy standard should be a certified reference material (CRM) or traceable to a standard reference material such as a NIST Standard Reference Material (SRM). Federal regulations require State And Local air monitoring agencies to perform annual accuracy checks.

Table 1. Function of Valves for Varian GC 3600CX System

<u>Relay #</u>	<u>Function</u>	<u>Event</u>	<u>Rotation</u>
1A	Sx Flow Off	-1	Counterclockwise
Delayed	Sx Flow On	+1	Clockwise
1B	Fixed Loop/vac. Off	-1	Counterclockwise
	Fixed Loop/vac. On	+1	Clockwise
1C	MFC/vac. Off	-1	
	MFC/vac. On	+1	
2A*	Ports 1-16	-2	Counterclockwise
	Ports 17-32	+2	Clockwise
3A	Fixed Loop/load	-3	Counterclockwise
	Fixed Loop/inject	+3	Clockwise
3B	MFC/Line purge	-3	Counterclockwise
	MFC/Load trap	+3	Clockwise
3C	Normal Operation	-3	Counterclockwise
	Canister Press. Test	+3	Clockwise
4A	Trap in Series	-2	Counterclockwise
	Trap bypass	+2	Clockwise
4B	Trap to Detector	-4	Counterclockwise
	Sample to Trap	+4	Clockwise
4C	Pressure test on	-4	
	Pressure lines	+4	
MA&MB	Fixed LoopSampling		
	MFC Sampling		

*No longer configured to be evoked by event number two. The default setting for valve 2A is set for ports #1-16.

Table 2. List of Valve Actuators for Varian GC 3600CX System

<u>Relay #</u>	<u>Number of Valve Ports</u>	<u>Actuator Rotation</u>	<u>Description</u>
2A, 3C	3	120°	
4A	4	90°	
1A-D, 3A & B M-B	6	60°	
M-A	8	45°	

GSV: Gas Sampling Valve; Sx: Sample

Table 3. Quality Control parameters-MLD024
Propane Multipoint Calibration Analysis

PROPANE - MULTIPOINT CALIBRATION AND LINEAR RANGE CALCULATION
 1998 TOTAL NMOC ANALYSIS - INSTRUMENT B

CALIBRATION STANDARD: CLM-09772
 CERTIFIED 1997 EXPIRES AUGUST 22, 2000

PROPANE ANALYSIS DATE : June 09, 1998

Linear Range: 1750 ppb C

ppbC =>	125.0	375.0	750.0	1125.0	1500.0	1750.0
Vol(cc) =>	50	150	300	450	600	700
Area (ac) =>	ac	ac	ac	ac	ac	ac
1st Run	24481	71254	140066	209258	276826	314743
2nd	24299	71495	140431	212425	281492	321125
3rd	24865	73524	140103	212877	282382	329569
4th						
5th						
Mean (ac) =	24548	72091	140200	211520	280233	321812
Std.Dev (ac)	288.9	1246.9	200.9	1971.9	2984.2	7436.9
% RSD =	1.18	1.73	0.14	0.93	1.06	2.31
#Obs. =	3	3	3	3	3	3

Conc. ppbC	Estimated AC	AC
-14.81	-4.219E-15	
0	2721.76	

125.0	24548	25701
375.0	72091	71660
750.0	140200	140598
1125.0	211520	209537
1500.0	280233	278475
1750.0	321812	324434

**** Regression Output:

Constant	2721.8
Std Err of Y Est	1973.0
R Squared	0.99977
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	183.84
Std Err of Coef.	1.39
R Correlation Coefficient	0.99989

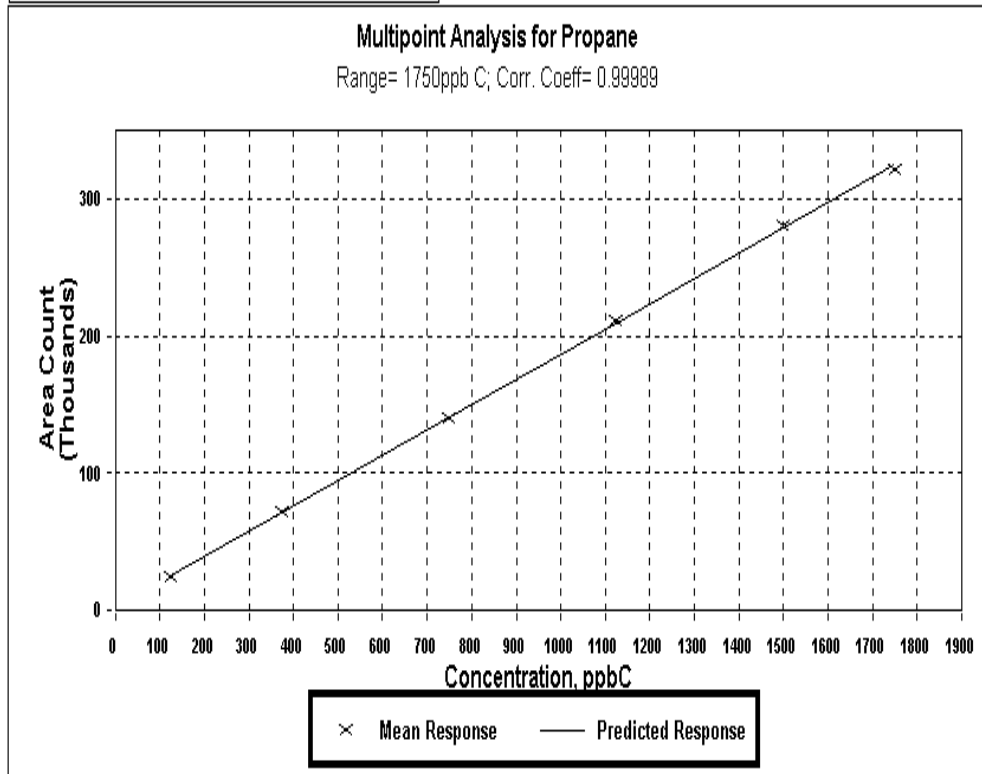


Table 4. LOD Calculation – MLD024

Propane NIST 09772

LOD Calculation for Total PDFID (MLD024) - 1998

Operator/Vol.	NIST Std. NIST9772	Date	NIST9772 Propane [] ppbC
JHB 300cc	Diluted	6/11/98	94.90
JHB 300cc	Diluted	6/11/98	86.92
JHB 300cc	Diluted	6/11/98	94.59
JHB 300cc	Diluted	6/11/98	84.55
JHB 300cc	Diluted	6/11/98	84.87
JHB 300cc	Diluted	6/11/98	86.84
JHB 300cc	Diluted	6/11/98	85.40
JHB 300cc	Diluted	6/11/98	86.99
JHB 300cc	Diluted	6/11/98	87.64

	Propane
Mean	88.08 ppbC
STD	3.923 ppbC
n	9
* 2.896X STD	12.317 ppbC
	Propane
LOD	12.3 ppbC

* 2.896 is the student T multiplier for 99% confidence for 9 values

Table 5. QC Parameters for Control A and Control B- MLD024

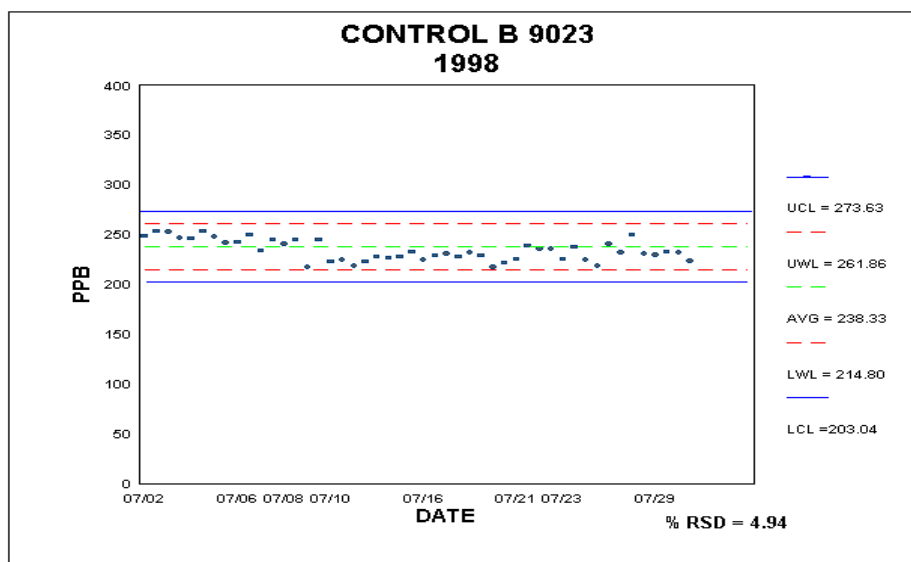
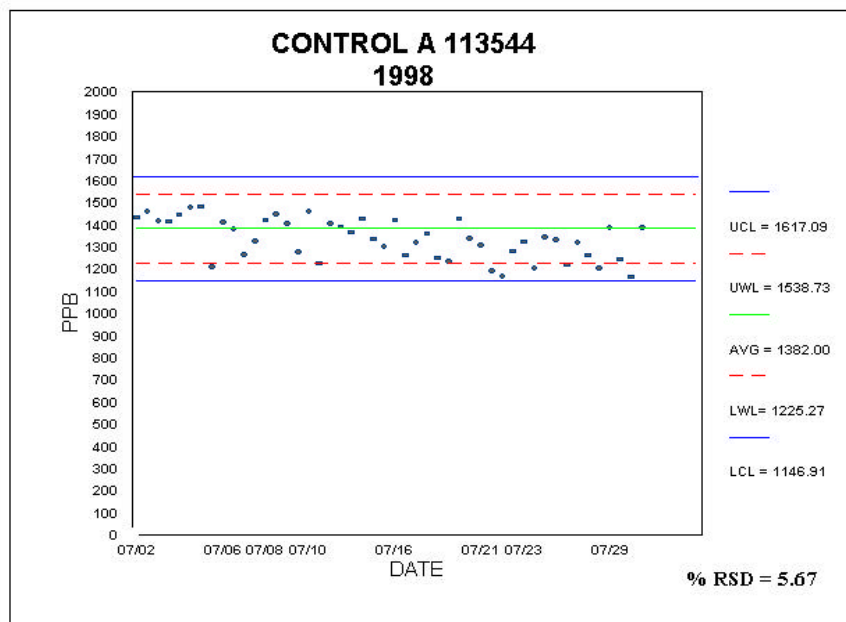


Figure 1. Varian 3600Cx GC Analytical System
MLD 024-Total PDFID

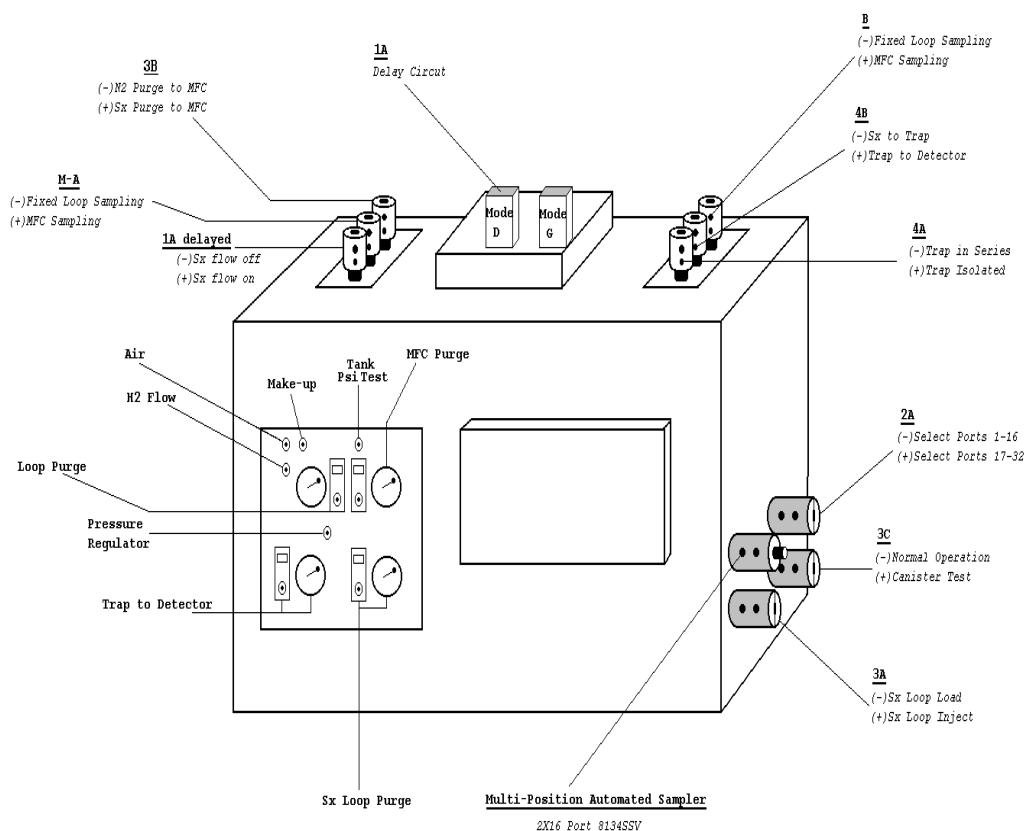
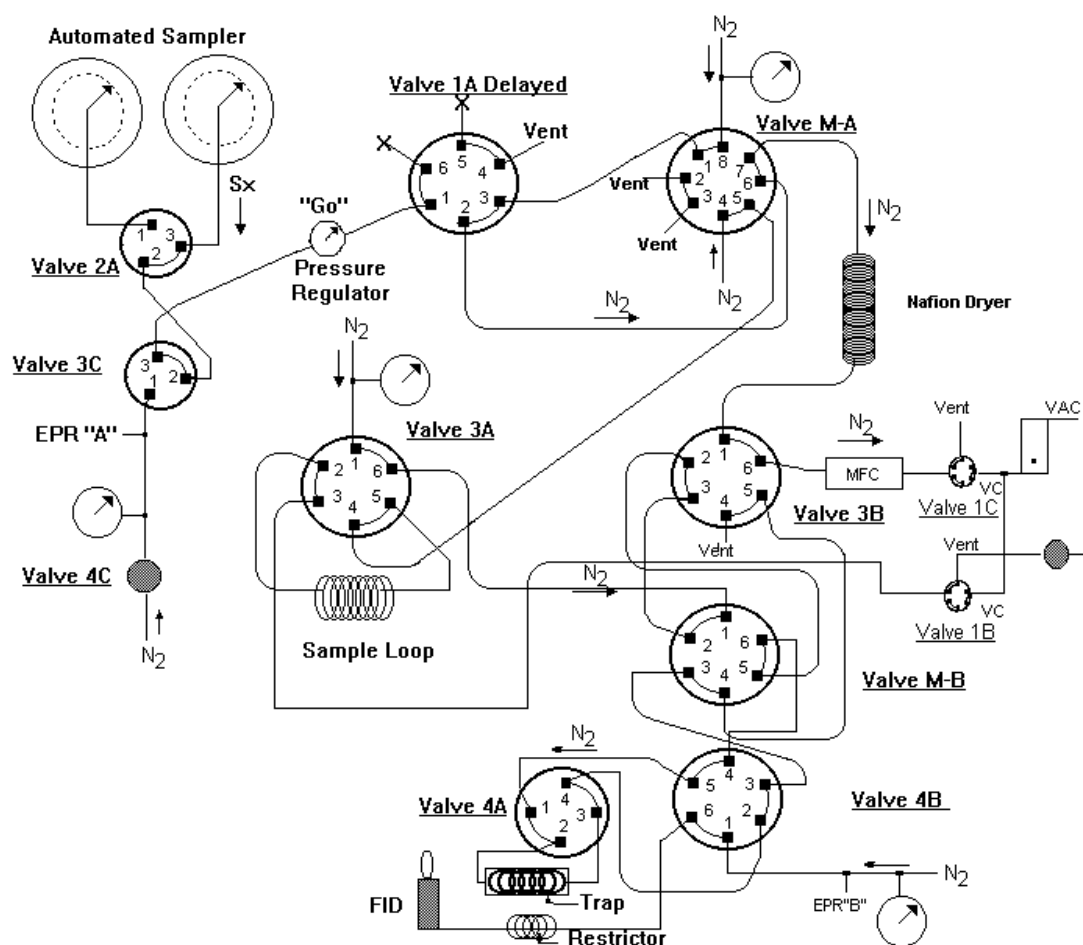


Figure 2A. Pre-Injection Time Events

Pre-injection system configuration: **Time=0.00 Min**

* Normal Operation – valve 3C is off, (-)

* MFC Sampling – Valves M-A/M-B are on, (+)



- * All events are off (-)
- * Sample flow dead ends
- * Nitrogen purges the system

Figure 2A: Time: 0.00min – All events are off

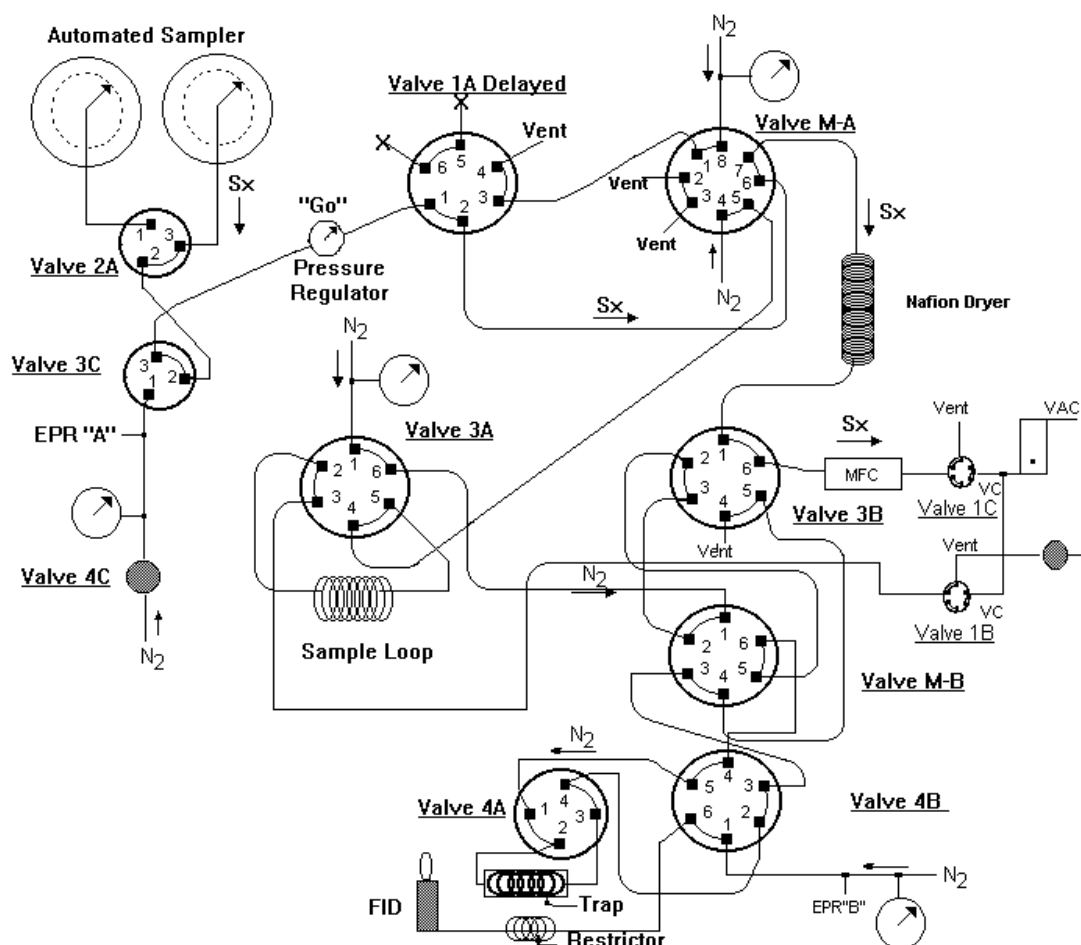
Figure 2B. Pre-Injection Time Events

Pre-injection system configuration: **Time = 0.01min**

* Normal operation – Valve 3C is off, (-)

* MFC sampling- Valves M-A/M-B are on, (+)

* Valve 1A, *Delayed*, is on (+)



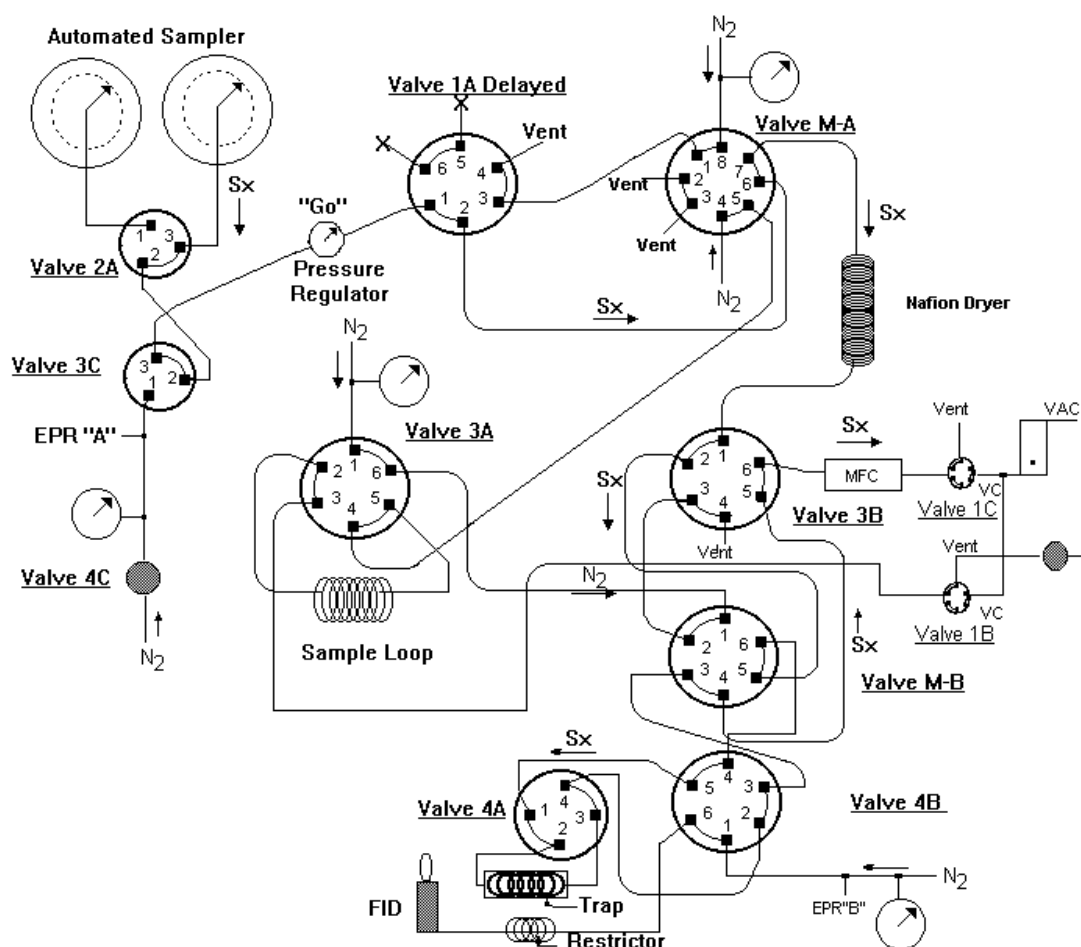
*Sample flow is directed through MFC

Figure 2B: Time: 0.01min – Valve 1A, *Delayed*, is on (+1)

Figure 2C. Pre-Injection Time Events

Pre-Injection system configuration: **Time = 1.00 min**

- * Normal operation – 3C is off, (-)
- * MFC sampling – Valves M-A/M-B are on, (+)
- * Valves 1A and 3B are activated, (+)



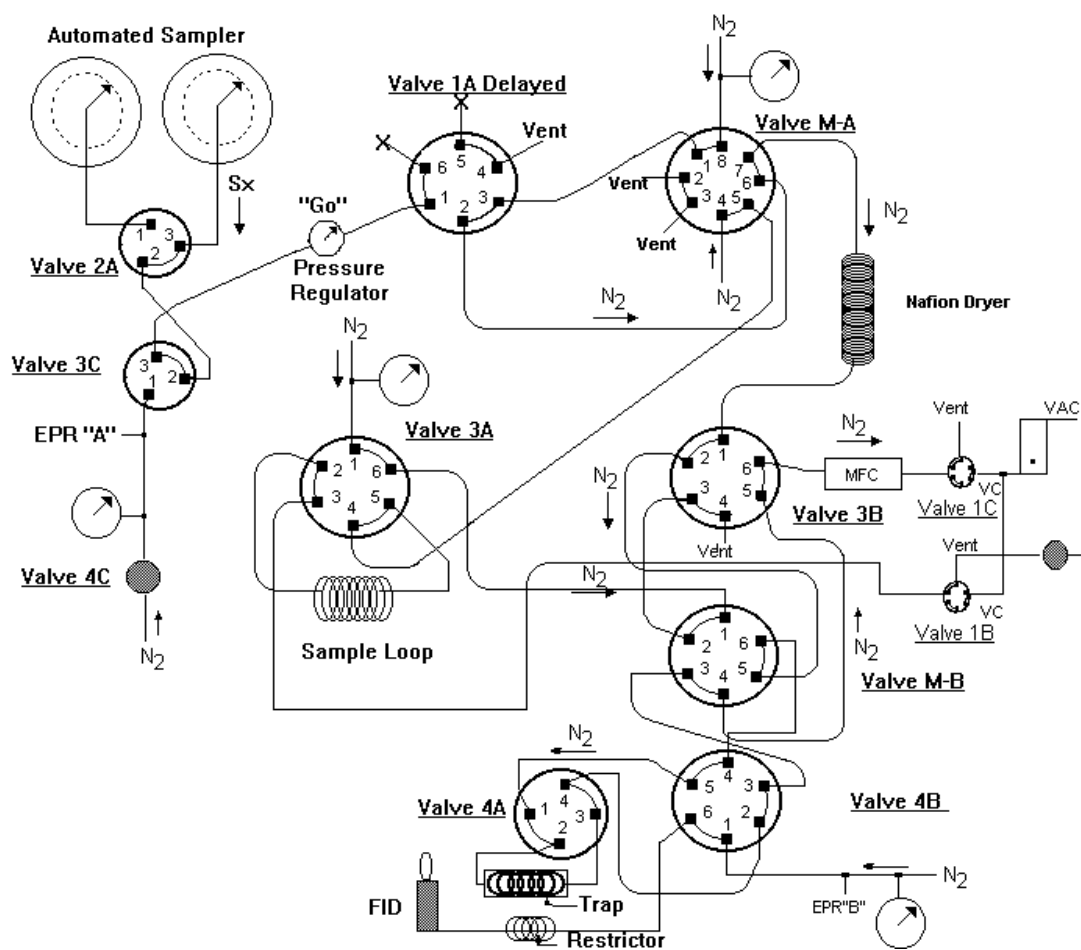
- * Sample flow is directed to the trap
- * The effective sample loading is initiated at this time

Figure 2C: Time: 1.00min –Valves 1A and 3B are on

Figure 2D. Pre-Injection Time Events

Pre-Injection system configuration: **Time=7.00 min**

- * Normal operation – 3C is off (-)
- * MFC Sampling – Valves M-A/M-B are on (+)
- * Valve 3B is on (+), Valve 1A, *Delayed*, if off, (-)



- * Sample flow dead ends
- * Nitrogen purges the trap
- * The effective sample loading is terminated

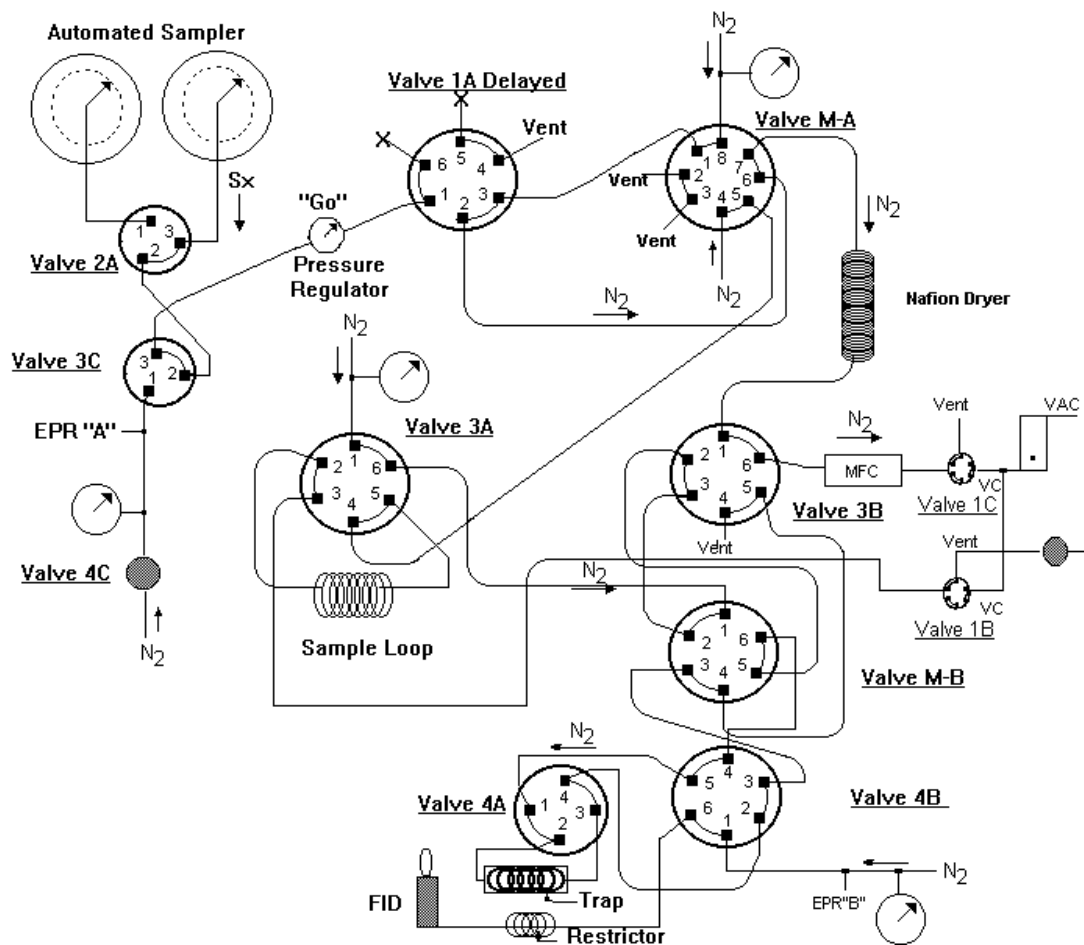
Figure 2D: Time: 7.00min – Valve 3B is on, Valve 1A is off

Figure 2E. Pre-Injection Time Events

Pre-Injection system configuration: **Time = 7.20 min**

* Normal operation – Valve 3C is off, (-)

* MFC sampling – Valves M-A/M-B are on, (+)



* All events are off, (-)

* Trap is heated to 190°C

Figure 2E: Time: 7.20min – End of Pre-Injection time events

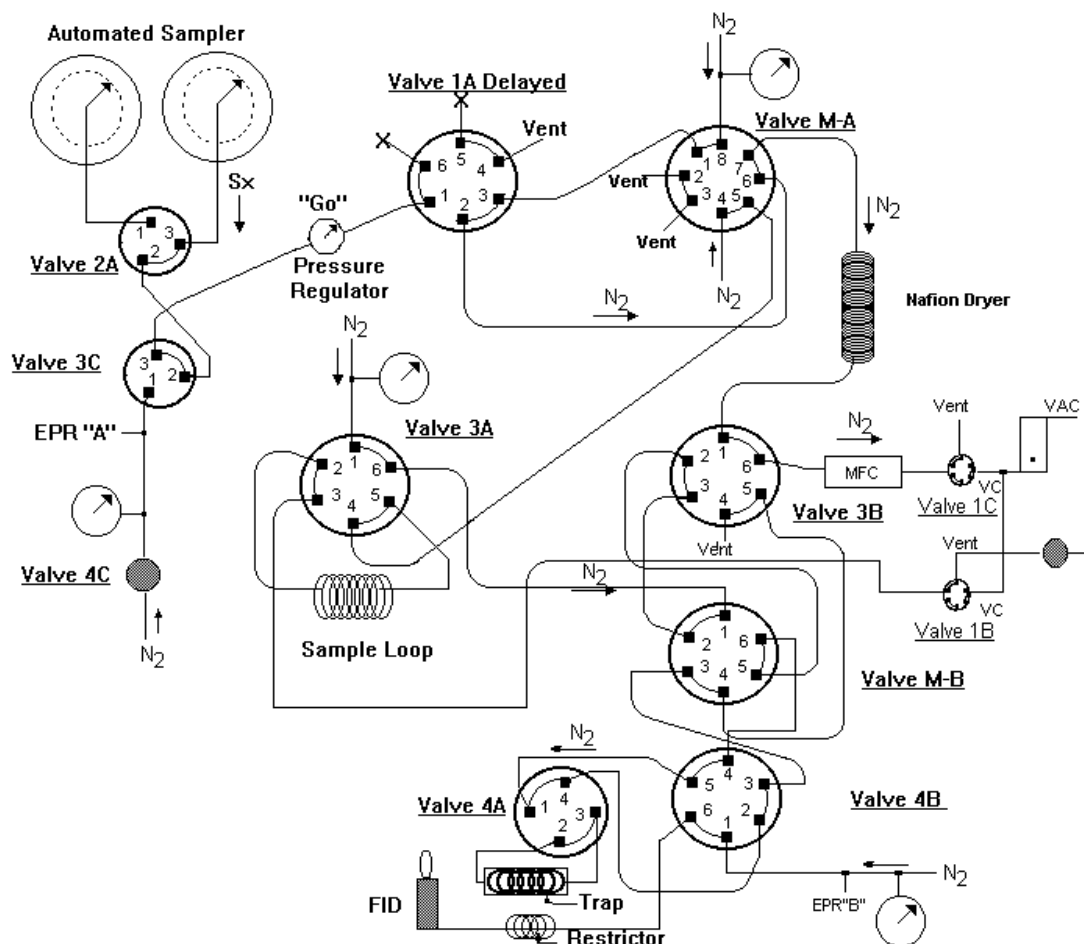
Figure 3A. Post-Injection Time Events

Post-Injection system configuration: **Time = 0.01 min**

* Normal operation – Valve 3C is off, (-)

* MFC Sampling – Valve M-A/M-B are on, (+)

* Valve 4A is on, (+)



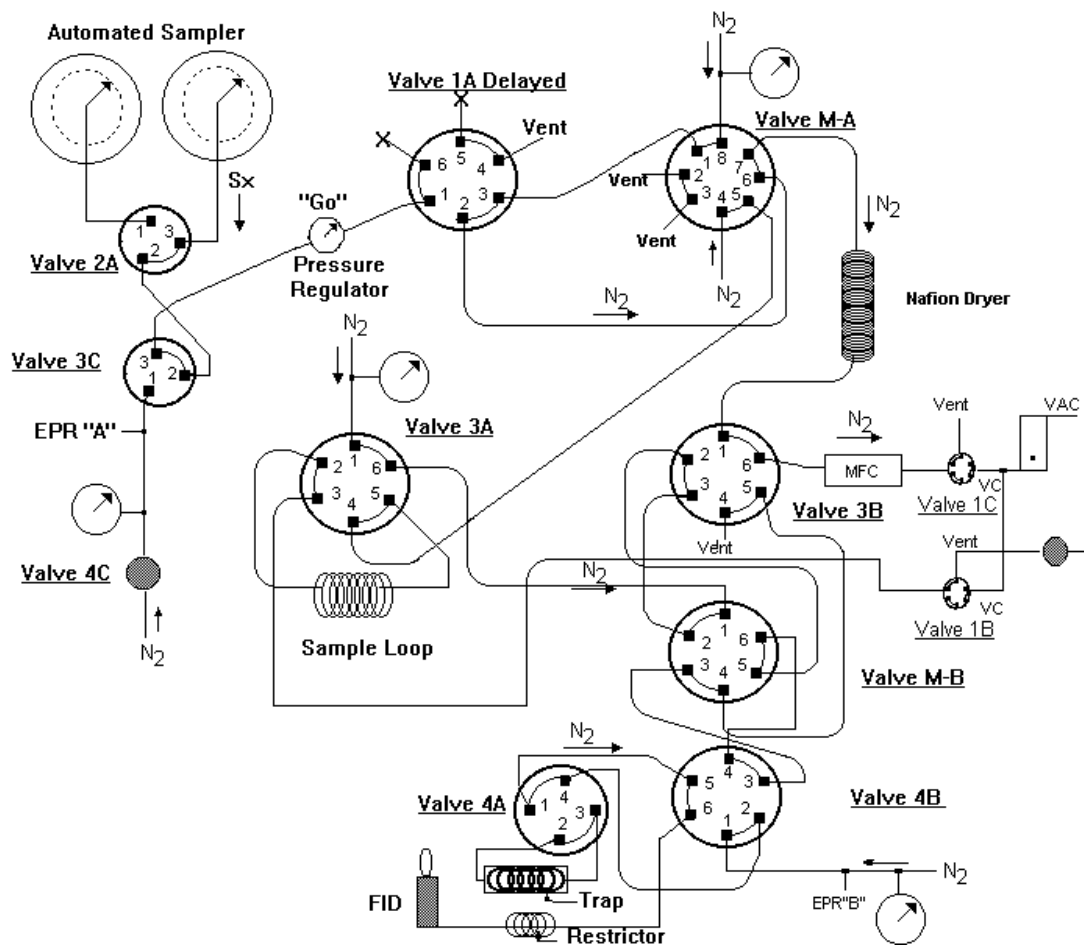
* Trap is isolated
* Trap is heated to 190°C

Figure 3A: Time: 0.01min Valve 4A is activated (+2)

Figure 3B. Post-Injection Time Events

Post-Injection system configuration: **Time = 1.00 min**

- * Normal operation – Valve 3C is off, (-)
- * MFC sampling – Valves M-A/M-B are on, (+)
- * Valve 4B, is activated, (+)



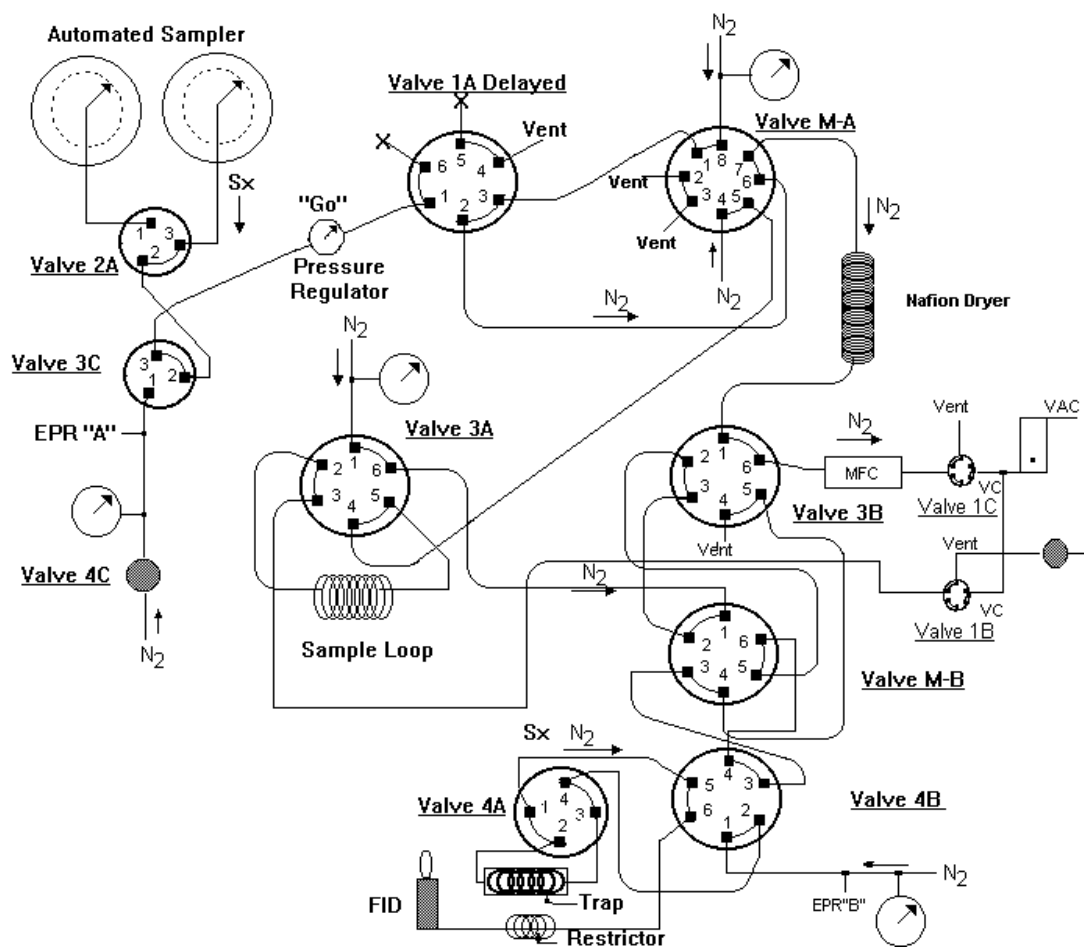
- * Trap is isolated
- * Trap is heated to 190°C
- * Nitrogen purge gas is redirected to purge the trap

Figure 3B: Time: 1.00min Valve 4B is activated (+4)

Figure 3C. Post-Injection Time Events

Post-Injection system configuration: **Time=2.00 min**

- * Normal operation – Valve 3C is off, (-)
- * MFC Sampling – Valves M-A/M-B are on, (+)
- * Valve 4A is off, (-)
- * Valve 4B is on, (+)



- * Trap is in series
- * Nitrogen purging the sample to the detector (FID)

Figure 3C: Time: 2.00min Valve 4A is off (-2)

Figure 4. Injector B Temperature Conversion

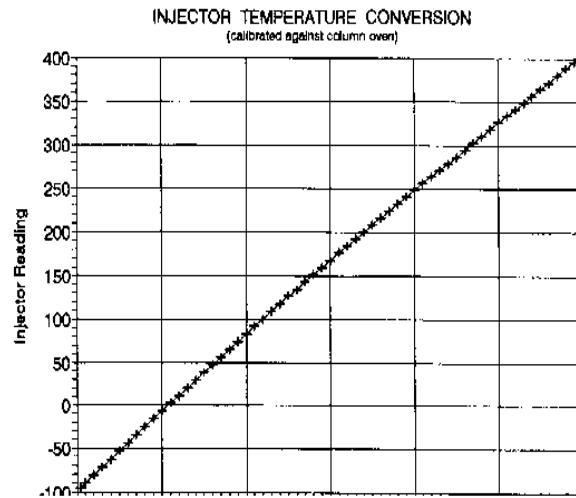


Figure 5. Interconversion of Concentrator Trap true temperature and Injector Setting

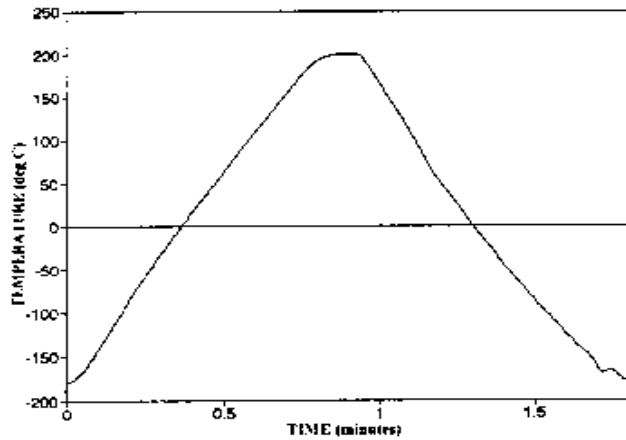


Figure 6. Propane Standard (750 ± 9 ppbC)
NIST Traceable Hydrocarbon Mix
CLM-09772

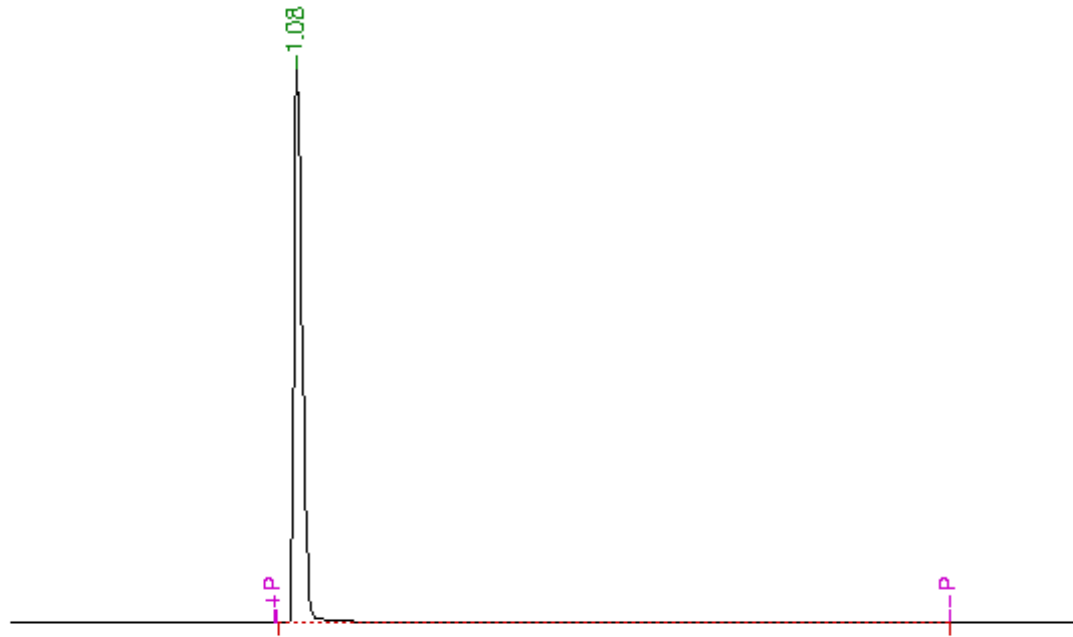
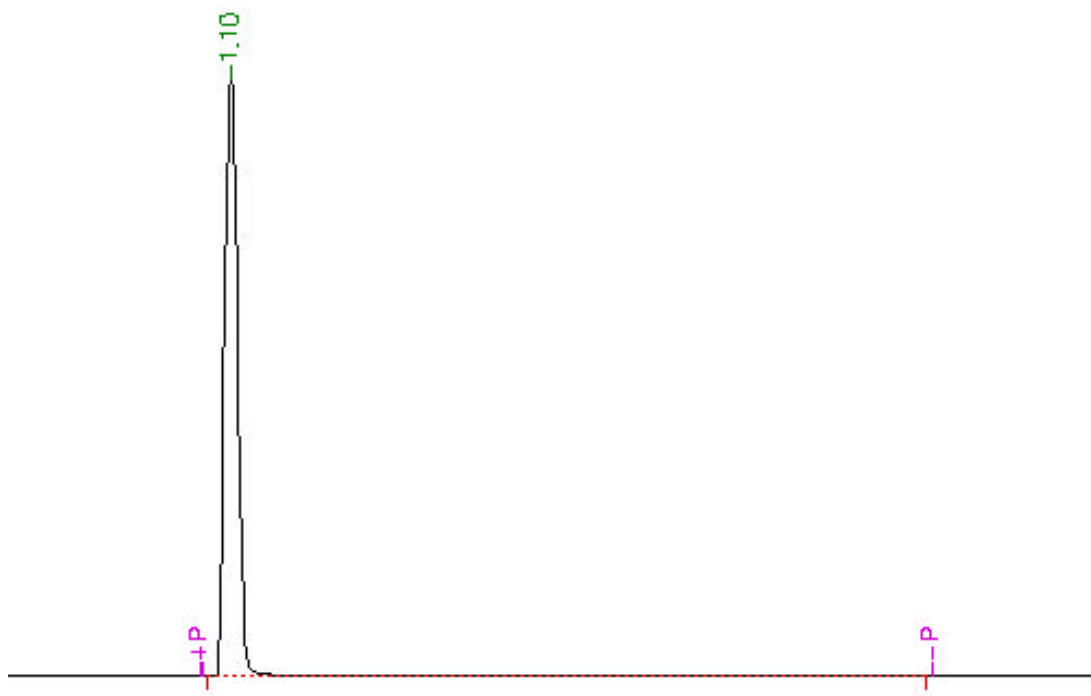


Figure 7. Ethane (1500 ppbC)
CC113544



APPENDIX I

TURBOCHROM – NELSON 2700 DATA SYSTEM

TURBOCHROM CHROMATOGRAPHY SYSTEM by PE Nelson: Turbochrom (Ver. 4.1<2F12>) is Microsoft Windows spreadsheet driven system, that has been installed on SCANDIUM PC (Pentium 133). To access Turbochrom, open the Navigator by double-click on the Navigator icon in the Turbochrom program group. The Navigator window is a graphical representation of the major functions in Turbochrom:

Instrument:	Instrument_(TPDFID)
Sequence Build:	mmddt.seq (eg. oc10t represents the sequence created for October10)
Method Build:	pdfid16.mth
Setup Analysis:	Edit instrument setup Edit data collection Modify the active mth, seq
Run Menu:	Controls single or multiple runs
Graphic Edit:	Appends pdfid 16.mth with *.raw file
View Menu:	View data points in real time
Reprocess:	Reprocess *.raw data files with pdfid16.mth
Application Menu:	Access any add-on application, TC2ASCII
Help Menu:	Help on Turbochrom

INSTRUMENT

An instrument, TPDFID, is configured to the PE Nelson 2700 system. System Configuration window (Config Icon), which allows you to edit the **F**ile menu (edit default printer), **C**olors command (defines colors for various screens), **I**nstrument command (edit configuration of all instruments connected to the computer), **P**ath menu (define where the data, methods and sequence can be stored), and **O**ptions menu (preferences in Graphic Method Editor, initialization of any 900 Series Interface). The Configuration summary for the instrument in the SCANDIUM PC is as follows:

Instr. No.	IEEE Add.	Instr. Type	Instr. Name	Autosampler Type
1	1	PEN900	TPDFID	None
2	2	PEN900	PDFID_18	None

There are three types of paths configured for each instrument:

1. System path: path names of directories that Turbochrom searches to find method

and sequence files

2. Program path: drive and directory where the configuration, program, and library files are located
3. Component defaults path: DEFAULT.CMP files that contains default values that Turbochrom uses for editing new components to the method

Paths

Program Path:	C:\TC4-2F12
System Path1:	C:\TC4-2F12\DATA16
System Path 2:	C:\TC4-2F12\DATA18
Component defaults path:	C:\TC4-2F12

Options

Initialize A/D's On Startup:	No	Confirm Polt Scale:	No
Header On Every Plot Page:	No	Display Reference Plot:	Yes
Default Plot Style:	Lines	Reference Plot Size (%):	15

FILE NAME FORMAT

The Nelson 2700 system (Turbochrom) uses 7 characters to form the file base name, three of which are reserved for numbering the data files. One can edit the **MMDD***** (i.e., **JN12**), and Turbochrom will append the cycle number for each analysis (i.e., **001**). To ensure that the base file name is unique and is indicative of the instrument that is generating the raw data file, 4 characters are used to form the file base name. The cycle of injection number is generated by Turbochrom and the data files are stored on the specified drive and subdirectory. The same base name is used for storing (*.RAW) and result (*.RST) files, where the three character extension differentiates one file from another. To prevent any confusion and to allow easy identifciation of data, the following naming convention will be used:

1. Use only a 4 character base name for data runs.
2. The first two characters will be a month code.
3. The third and fourth characters will be a date code.
4. The fifth through seventh character represents the sample number for the base name.

Month codes

JAN = JA	JUL = JL
FEB = FB	AUG = AU
MAR= MR	SEP = SE
APR = AP	OCT = OC
MAY= MY	NOV = NO
JUN = JN	DEC = DE

Example: SE08004 would be September 8th, Method pdfid16, cycle/injection number 4.

SAMPLE NAME FORMAT:

Within a sequence or during a manual download you must enter a sample name. The format for sample name is as follows:

Generally a system blank or a sample of Grade 5 Nitrogen or equivalent is run as the first sample of the day to insure that the system is free of contamination.

Enter a system blank as: **BLK**

Next, label a calibration propane standard with a certified value of 750 ppb C as: **STD 9772**. Next, Ethane at nominal value of 1500 ppb C is labelled as: **CTRLA 113544**. The last control sample before the ambient analysis should be a low level, hydrocarbon gas mix, of a nominal value of 244 ppb C. This sample is entered as : **CTRLB 9023**

Samples, which have been logged into LIMS and will be transeferred, use 9 characters for the LIMS number. The LIMS number itself will be limited to 8 characters and the 9th character is used as a replicate code. If this is left blank, it represents the first replicate. A-J represents the 2nd through 10th replicates. The first characters must be NM for ambient samples and CC for contamination check samples. After the 9th character, enter a space and then type in the sample location or other information. For example the duplicate of a Bakersfield sample having a LIMS number of NM002345 would be entered as: **NM002345A BF**

If the ninth character is not used (i.e. the sample is not a replicate), insert two spaces after the LIMS number before entering the sampling site.

Turbochrom Method

Turbochrom Method File: C:\TC4-2F12\DATA16\PDFID16.MTH

Created by :SSR On: 7/28/97 11:46 AM
Edited by :SLT On: 1/7/98 08:22 AM
Description :PDFID – Total NMOC analysis on Varian 3600 GC

Number of Times Edited: 2
Number of Times Calibrated: 200

Instrument Conditions :

SCM – 6/176/97 – Changed input voltage for interface to 1 mv from 10 mv; changed sampling rate to 4.00 pts/s from 1.25 pts/s; set NT to 1 μ v and AT to 10.00 μ v;

Instrument Control Method :

Instrument name : TPDFID

Interface Parameters :

Delay Time : 0.00 min.
Run Time : 4.30 min.
Sampling Rate : 4.0000 pts/s
Interface Type : 900
Analog Voltage Input : 1000 mV
Data will be collected from channel A

Timed Events :

There are no timed events in the method

Real Time Plot parameters :

Channel A -- Pages : 1 Offset : 5.000 mV Scale : 30.000 mV
Channel B -- Pages : 1 Offset : 0.000 mV Scale : 1000.000 mV

Processing Parameters:

Bunch Factor : 1 points
Noise Threshold : 1 μ V
Area Threshold : 10.00 μ V

Peak Separation Criteria

Width Ratio : 0.200
Valley-to-Peak Ratio : 0.010

Exponential Skim Criteria

Peak Height Ratio : 5.000
Adjusted Height Ratio : 4.000
Valley Height Ratio : 3.000

Baseline Timed Events:

Event #1 - -P at 0.013
Event #2 - +P at 1.015
Event #3 - +I at 1.017
Event #4 - +M at 1.038
Event #5 - -M at 2.075
Event #6 - -P at 2.091

Annotated Replot Parameters:

Offset will be autozeroed
Plot Scale : 30.000 mV
Number of Pages : 1
Plot Title : Total NMOC by TPDFID
X-Axis Label : Time [min.]
Y-Axis Label : Response [mV]
Orientation : Landscape

Retention Labels : Top of Plot
Component Labels : Actual Time
Automatically set plot start and end times to data limits

Report Format Files:

No report format files given

User Programs:

No user programs will be executed

Global Information:

Default Sample Volume : 1.000 ppb C
Quantitation Units : ppb C
Void Time : 0.000 min
Correct amounts during calibration : YES
Reject outliers during calibration : NO
An External Standard calibration will be used
Unknown peaks will use the response factor of the nearest reference peak

Component Information:

Total NMOC

Component Type : Timed Group
Start Time : 1.005 min End Time : 3.000 min

Reference Component:

Calibrating Area versus Amount using a Pt. To Pt. Fit

Curve will ignore the origin

Amounts will not be scaled prior to the regression

Weighting factor for the regression : None

User Values:

Label	:	
Value 1	:	0.000000
Value 2	:	0.000000
Value 3	:	0.000000
Value 4	:	0.000000
Value 5	:	0.000000

Calibration Levels:

Level Name	Amount	Area	Height	ISTD Resp.	ISTD Amt.	# Replicates
level 1	750.0000	141279.90	83930.16	-----	-----	1

Calibration Replicate Lists :

Component : Total NMOC

Level : level 1

Area	Height	Vol Adj Amt	ISTD Response	ISTD Amount	Date/Time	File
141279.00	83930.16	750.0000	-----	-----	1/7/98 08:21AM	SE12004

SEQUENCE

Turbochrom Sequence File: C:\TC4-2F12\DATA16\SE12T.SEQ

Created by : SSR

On: 9/12/97 07:46 AM

Edited by : SST

On: 9/12/97 12:06 PM

Number of Times Edited: 1

Sequence File Header Information:

Number of Rows : 4

Instrument type : 760 / 900 Series Intelligent Interface

Injection Type : SINGLE

Sequence Sample Descriptions- Channel A

Row	Type	Sample Name	Sample Number	Study Name	Sample Amount	ISTD Amount	Sample Volume	Dil. Factor	Mult	Divisor	Addend
1	Sample	BLK	1	pdfid16	1.000	1.000	1.000	1.000	1.000	1.000	0.000
2	Sample	STD9772	2	pdfid16	1.000	1.000	1.000	1.000	1.000	1.000	0.000
3	Sample	CTRLA	3	pdfid16	1.000	1.000	1.000	1.000	1.000	1.000	0.000
4	Sample	CTRLB	4	pdfid16	1.000	1.000	1.000	1.000	1.000	1.000	0.000

*Sequence Sample Description – Channel A

Row	Site	Rack	Vial	Inst Method	Process Method	Calib Method	Report Format	Raw File	Result File	Modified Raw File	Cal Rpt	Level Name	Updat RT
1	-	1	1	pdfid16	pdfid16	pdfid16	pdfid16	SE12001	SE12001	SE12001	-	-	-
2	-	1	2	pdfid16	pdfid16	pdfid16	pdfid16	SE12002	SE12002	SE12002	-	-	-
3	-	1	3	pdfid16	pdfid16	pdfid16	pdfid16	SE12003	SE12003	SE12003	-	-	-
4	-	1	4	pdfid16	pdfid16	pdfid16	pdfid16	SE12004	SE12004	SE12004	-	-	-

* Please note that there is no entry for Baseline File, which is left out due to insufficient space.

REPORT FORMAT FILE

Turbochrom Report Format File – C:\TC4-2F12\DATA16\PDFID16.RPT

Created by : SSR On: 6/17/98 02:04 PM
Edited by : SSR On: 08/26/98 01:17 PM
Number of Times Edited: 1

Report Title:

PDFID Inst. B (Lotus/Varian). PDFID.MTH 8/26 #3 jhb

User Report Header:

No user header will be printed

User Report Footer:

No user footer will be printed

Report Format Options:

System Header

A medium default header will be printed

Compressed mode

The report body will be in 132 column mode

Report Body Options

Identified components

Identified timed groups

Unidentified peaks

Missing components will be listed in a separate report

Missing timed groups

Miscellaneous Options

Expand timed groups

Print missing component report

Formfeed between reports

Report Area Reject = 0.00

Report Columns:

Column	: 1 – Peak Number	Width	: 3
Label 1	: 'Peak'	Label 2	: '#'
Precision	: 0 Total Column: NO	Expression	:
Column	: 2 – Component Name	Width	: 20
Label1	: 'Component'	Label 2	: 'Name'
Precision	: 0 Total Column: NO	Expression	:

Column	: 3 – Retention Time	Width	: 7
Label 1	: 'Time'	Label 2	: '[min]'
Precision	: 3 Total Column : NO	Expression:	
Column	: 4 – Raw Amount	Width	: 10
Label 1	: 'Raw Conc.'	Label 2	: 'ppb C'
Precision	: 2 Total Column : YES	Expression	:
Column	: 5 -- Adjusted Amount	Width	: 10
Label 1	: 'Conc.'	Label 2	: 'ppb C'
Precision	: 2 Total Column : YES	Expression	:
Column	: 6 – Peak Area	Width	: 11
Label 1	: 'Area'	Label 2	: '[μV s]'
Precision	: 2 Total Column : YES	Expression	:
Column	: 7 – Peak Height	Width	: 9
Label 1	: 'Height'	Label 2	: '[μV s]'
Precision	: 2 Total Column : YES	Expression	:
Column	: 8 – Baseline Code	Width	: 3
Label 1	: 'BL'	Label 2	:
Precision	: 0 Total Column : NO	Expression	:
Column	: 9 – Area to Height Ratio	Width	: 6
Label 1	: 'Area/Height'	Label 2	: '[s]'
Precision	: 2 Total Column : NO	Expression	:

APPENDIX II

I. GAS CHROMATOGRAPHY

A. Gas Chromatographic Methods

Gas chromatographic (GC) methods are highly sophisticated microanalytical procedures. They should be used only by analysts experienced in the techniques required and competent to evaluate and interpret the data.

1. Gas chromatograph:

a) Principle

In gas chromatography a mobile phase (a carrier gas) and a stationary phase (column packing or capillary column coating) are used to separate individual compounds. The carrier gas is nitrogen, argon-methane, helium, or hydrogen. For packed columns, the stationary phase is a liquid that has been coated on an inert granular solid, called the column packing, that is in borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven, and detector is maintained. Stationary-phase material and concentration, column length and diameter, oven temperature, carrier-gas flow, and detector type are the controlled variables. When the sample is introduced into the column, the organic compounds are moved through the column by carrier gas. They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phases.

b) Interferences

Some interferences in the GC analysis occur as a result of sample or carrier gas contamination, or because large amounts of a compound injected into the GC, linger in the detector. Methylene chloride, chloroform, and other halocarbon and hydrocarbon solvents are ubiquitous contaminants in environmental laboratories. Strenuous efforts should be taken to isolate the analytical system from laboratory areas where these or other solvents are in use. Sources of interference originating in the chromatograph, and countermeasures, are as follows:

* Septum bleed – This occurs when compounds used to make the septum on the injection port of the GC bleed from the heated septum. These high-molecular-weight silicon compounds are distinguished readily from compounds normally encountered in environmental samples. Nevertheless, septum bleed can be minimized by using septum sweep in which clean carrier gas passes over the septum to flush out the “bleed” compounds.

- * Column bleed – This term refers to the loss of column coating or the breakdown of products when the column is heated. This interference is more prevalent in packed columns, but also occurs to a much lesser extent in capillary columns. It occurs when the column temperature is high or when water or oxygen is introduced into the system. Solvent injection can damage the stationary phase by displacing it. Certain organic compounds acting as powerful solvents, acids, or bases can degrade the column coating. Injection of large amounts of certain surface-active agents may destroy GC columns.
- * Ghost peaks – These peaks occur when an injected sample contains either a large amount of a given compound, or a compound that adsorbs to the column coating or injector parts (e.g., septum). When a subsequent sample is injected, peaks can appear as a result of the previous injection. Eliminate ghost peaks by injecting a more dilute sample, by producing less reactive derivatives of a compound that may interact strongly with the column material, by selecting a column coating that precludes these interactions, or by injecting solvent blanks between samples.

2. Detector:

Various detectors are available for use with gas chromatographic systems. Only flame ionization detector (FID) is used in this method.

The FID is widely used because of its high sensitivity to organic carbon-containing compounds. The detector consists of a small hydrogen/air diffusion flame burning at the end of a jet. When organic compounds enter the flame from the column, electrically charged intermediates are formed. These are collected by applying a voltage across the flame. The resulting current is amplified by an electrometer and then measured. The response of the detector is directly proportional to the total mass entering the detector per unit time and is independent of the concentration in carrier gas.

The FID is perhaps the most widely used detector for gas chromatography because of several advantages: 1) it responds to virtually all organic carbon-containing compounds with high sensitivity (approximately 10^{-13} g/ml); 2) it does not respond to common carrier gas impurities such as water and carbon dioxide; 3) it has a large linear response range (approximately 10^7) and excellent baseline stability; 4) it is relatively insensitive to small column flowrate changes during temperature programming; 5) it is highly reliable, rugged, and easy to use; and 6) it has low detector dead volume effects and a fast response. Its limitations include: 1) it gives little or no response to noncombustible gases and all noble gases; and 2) it is a destructive detector that changes the physical and chemical properties of the sample irreversibly.

APPENDIX III VARIAN STAR CHROMATOGRAPHY WORKSTATION

The Varian Star Chromatography Workstation operates under MS-DOS and uses Microsoft Windows 95. The Workstation controls the instruments, automates data collection and analysis, and documents the results of a chromatographic run. It uses four primary applications to perform specific tasks:

1. System Control and Automation
2. Method Editor
3. Interactive Graphics and Data Handling
4. Reports

The Interactive Graphics/Data Handling and Report Generating will not be addressed here since PE Nelson 2700 Data System (Turbochrom) is the primary interactive software used at this time. Also, the scope of Appendix III is directed only for TPDFID analysis and only addresses set parameters for Method MLD024. For general application of Star Workstation software, please refer to the Star Chromatography Workstation Operation Manual, Varian Chromatography Systems (1993).

System Control and Automation: Part 1

This is the primary station for the instrument. It reports on the status of the instrument and on its configuration. It also allows you to run methods for a particular set of samples. From this window, one can access and edit three main types of files: method file (.MTH), sample file (.SMP), and sequence file (.SEQ).

The basic configuration for GC Star Workstation consists of up to four GC systems with one Analog-to-Digital Converter (ADC) Board installed for the PC for each GC (i.e., each GC is cabled to its own ADC Board). Before any sample injection can be made, the instrument must be properly configured. The bus address of each module, which appears at the bottom of its icon – the bus address of a GC (Instrument Control/Auto Control Module box) should always be one number greater than the bus address of its ADC Board.

Method MLD024 is configured with Varian 3600CX – TPDFID with Address 17 for the Auto Control Module and Address 16 for the ADC Board. To configure or to confirm the configuration of the instrument, open Varian Star 4.5 – System Control, click 'Instrument 1 Parameters' and set the following parameters:

Instrument: TPDFID
Operator: Your Name
Max Errors: 99 (number of non-fatal errors)
X Prompt on Sequence Start?

Wait until the AutoControl Module is activated, open System Control – TPDFID by double clicking on the AutoControl Module 3600, Address 17. This window provides

the current status of the instrument, and allow one to access, and to modify all the system parameters for a sample run.

Open 'File' Sequence File
 Method File
 SampleList File
 SampleLog File
 Printer Setup...
 Save Active Method...
 Exit

Open 'Method File'...
 New...
 Open...
 Activate...

Select New or Open depending upon whether method **pdfid74.mth** already exists as a file. By taking the steps listed above, the operator has entered into the Method Editor.
Note: Any of the 4 major functions can be accessed from another active function.

Method Editor:

A. Open pdfid74.mth: 1 ADC Board-Module 16
 2 ADCB Data Handling-Module 16.A
 3 ADCB Report-Module 16.A
 4 3600 GC-Module 17

1. **ADC Board-Module 16**

ADCB – Set Conditions (set end time for run)

<u>E</u> nd Time:	3.00 minutes
<u>C</u> hannel <u>A</u>	
<u>D</u> etector Name:	FID
<u>F</u> ullscale Value:	
<u>X</u>	Zero Display at Start
<u>C</u> hannel <u>B</u>	Not used

Detector Information Detector Bunch Rate: 16 points (2.5 Hz)
 Noise Monitor Length: 50 bunched points (20.0 sec)
 Data File Name: MMMDD*
 Number Files From: 1
 *MMM=month; DD=Day

2. ADCB Data Handling-Module 16.A

Integration Parameters

Peak Detection:	Initial S/ <u>N</u> Ratio (3) Initial Peak <u>w</u> idth (2 sec) Initial <u>T</u> angent (Height 10%)
Monitor Noise:	<u>B</u> efore every run
Peak Measurement:	Measurement Type (Peak <u>A</u> rea) Peak Result Calculation (Report <u>U</u> nidentified Peaks)

Peak Table

Retention Time:	2.070
Peak Name:	Non-Methane
Group:	0
Level 1 Amount:	750
Level 2 Amount:	1

Calibration Setup

Calibration Type:	<u>E</u> xternal Standard
Number of Calibration Levels:	10
Multi-Level Parameters:	<u>O</u> rigin (Force) <u>F</u> it (Linear)
Weighted Regression:	None
Replicate Treatment:	<u>K</u> eep Replicates Separate
Replicate Tolerance:	Always <u>a</u> dd new replicates (No Action if Out of Tolerance)
Calibration Range Tolerance:	<u>R</u> ange Tolerance (10.0%)
Out of Tolerance Action:	No Action

Edit/Lock Calibration Data:	Retention Time (2.070) Peak Name (Non-Methane) X (236.03)
-----------------------------	---

The entered values for X³, X², and Intercept are "0".

Verification Setup

<u>D</u> eviation Tolerance (%):	100.0
Out-of-Tolerance Action:	No Action

Time Events Table:

No Entry

1. ADCB Report-Module 16.A

Print Options

Print Copies:	1
Single Run Reports:	Print <u>C</u> hromatogram Print <u>R</u> esults

Result Format

Results Table:

Amount Units (PPBC)

Number of Decimal Digits (2)

Run Documentation:

Please check every item except Calibration Report

Chromatogram Format

Chromatogram Start and End:

Start Time (0 min)

End Time (1440.00 mins)

Time and Amplitude Scale:

Auto Scale

Length in Pages:

1

Time Tick Interval:

1.0 min

Please check all Chromatogram Annotations

Calibration Block Report Format:

Print Text and Curves

Show Outliers on Curve

- 4. Open 3600GC-Modules 17:** 3600 GC Injector
3600 GC Auxiliary
3600 GC Column
3600 GC Detectors
3600 AutoSampler
3600 GC Relays
3600 GC Stripchart

Edit each of the items listed for 3600 GC-Module 17 and set the parameters as listed in Section 6.02. The GC Relays Time Program is listed in Section 6.04.01.

B. Open Idle16.mth:

1 ADC Board-Module 16

2 ADCB Data Handling-Module 16.A*

3 ADCB Report-Module 16.A*

4 3600 GC –Module 17

*Not addressed in this method

Note: If idle16.mth does not exist, copy pdfid74.mth and edit only the following parameters listed below. Save method as **Idle16.mth**.

1. ADC Board-Module 16

Set Conditions

End Time: 20 mins

X Zero Displays at Start

Detector Information:

Detector Bunch Rate:

4 points (10.0Hz)

Noise Monitor Length:

64 bunched points
(6.4 sec)

Data File Name:

Star

Number Files From:

1

2. 3600 GC-Molecule 17

GC Injectors		Injector A	Injector B
Injector Type:		Isothermal	Temp. Programmable
Injector Heater:	Off		On
Initial Temperature:	150° C		150° C (<i>Actual Temp. 100° C</i>)
Hold Time (min.)			Infinite
Coolant to Injector:			Off
Injector Program End Time(min):			Infinite
3600 GC Auxiliary		Same as pdfid16.mth	
3600 GC Column:		Column O <u>u</u> en:	On
		Initial T <u>em</u> perature:	100°C
		H <u>o</u> ld Time:	Infinite
		Temperature Program:	Not Used
		Thermal S <u>t</u> abilization Time (min):	2.00
		GC Column Program End Time (min):	Infinite
		Coolant to C <u>o</u> lumn:	Off
3600 GC Detectors:		Same as pdfid74.mth	
3600 Autosampler:		Same as pdfed74.mth	
3600 GC Relays:		Relay Time Program: Do Not Use	
3600 GC Stripchart:		Same as pdfid74.mth	

System Control and Automation: Part 2

In the System Control-pdfid16T window, build a SampleList file and a Sequence file.

A. To set up/edit a SampleList File:

Under File, click SampleList File. Select SampleList (Type:8134 SSV)
pdfid16.smp.

SampleList or SampleFile list is required by System Control for identifying what kind of sample is being injected and the order of sample injection (when performing a series of injections). In the displayed 'pdfid16.smp-SampleList' window, there are the following parameters that need to be defined:

1. Sample Name
2. Sample Type
3. Cal. Level
4. # Inj.
5. Injection Notes
6. AutoLink
7. Stream
8. Relay Program
9. Amount Std.
10. Unidentified Peak Factor
11. Multiplier
12. Divisor

1. Sample Name: Use same format for base names as in PE Nelson 2700 Data System (Appendix I).
2. Sample Type: Use 'Analysis' as default for all samples. The system calibration and report generation will be done by PE Nelson 2700 Data System (Appendix I).
3. Cal. Level: Not applicable (NA) – all samples are set for analysis. Calibration is done by PE Nelson 2700 Data System (Appendix I).
4. # Inj.: Allows you to set the number of injections (i.e., number of analysis) to be performed on that particular sample.
5. Injection Notes: Record notes for each injection, if needed.
6. AutoLink: NA
7. Stream: Identify the port (stream) number for the corresponding sample.
8. Relay Program: Discussed below in text.
9. Amount Std: Use 1.0000 as a default value.
10. Unidentified Peak Factor: Use 0.0000 as a default value.
11. Multiplier: Use 1.0000 as a default value
12. Divisor: Use 1.0000 as a default value.

These values are set in the 'Defaults...' window (click on the defaults button in the SampleList window). These parameters are common to all

entries in the SampleList with the exceptions of Sample Name, #Inj., and Stream, which are edited directly in the SampleList window.

Relay Program:

In the 'Defaults...' window, click on 'Relays...' button and open '8134 SSV Relay Program'. A 300 cc aliquot of standard, control or ambient air sample is introduced into the GC from the automated preconcentration system by means of the relay time program set below:

<u>Time (min.)</u>	<u>Relay</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0.00		-	-	-	-
0.01		1	-	-	-
1.00		1	-	3	-
7.00		-	-	3	-
7.20		-	-	-	-

Note: (-) sign = off position

Save or update the default settings, and return to the 'pdfid16.smp – SampleList' window. Complete the sample list and Save.

To run a dilution of a particular sample or a multipoint analysis of Total PDFID analytes, edit the relay time program in the pdfid16.smp. as follows:

1. Identify the sample that requires dilution.
2. Identify the stream that the particular sample is attached to.
3. Enter the sample in the SampleList, using default parameters. Append "D" (dilution) to the front of the LIMS number (i.e. DNM_____ or DM_____) to avoid duplicate transfer from the peaksum.
4. Click on the stream number and edit the re-lays in the SampleList window. Do not edit the relays under the default window because these are set for 300 cc sample volume.
5. Edit the time between activating Valve#1 (**1**) and turning off Valve #1 (-), thus varying the effective sample loading. Leave other time events as default values.
6. Save the changes made., Only the selected stream will have saved edited parameters, whereas the rest of the samples in the SampleList file will have default values.
7. The result of the diluted sample is recalculated using the dilution factor, and the peaksum of the original run would be modified with the recalculated result.

Idle16.smp: Create an Idle SampleList file for Idle16.mth by using the default values and editing the relay program. Save as Idle16.smp.

<u>Time (min.)</u>	<u>Relay</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0.00	1	-	-	-	-

B. Edit New Sequence:

The Sequence (.seq) file is responsible for the coordination and execution of a number of operations. The .seq file consists of list of .mth file/.smp file pairs in order of execution. By using the .seq file, one can:

1. Run each SampleList using a different method
2. Run a series of SampleLists using the same method
3. Run one SampleList run by a variety of methods

In the new Sequence window, click on desired cell in the column. The default path is displayed with a file name that is highlighted. Either type in the path name or use a Browse button. The typical .seq for Total pdfid16T run is shown below:

<u>Method</u>	<u>SampleList/Log</u>	<u>Action</u>
1. C:\Star\pdfid74.mth	C:\Star\pdfid16.smp	Inject
2. C:\Star\ldle16.mth	C:\Star\ldle16.smp	Inject

Select the File and Save As...pdfid16.seq. To activate a sequence, click File/Sequence File/Activate. If "Activate" is not an available option, stop automation, and then activate the desired sequence. Select pdfid16.seq, a System Control Sequence dialog box appears.

When a sequence is started, System Control performs a series of checks on the method and SampleList files. If any of these checks fails, System Control aborts the seq and indicates the cause within message boxes or entries to the Sequence Log.

ADDENDUM

Quick Reference Guide for the Total PDFID Analysis

1. **Check all the connections and support gases for the instrument. Make sure that all the valves are connected and opened. None of the major support gas cylinders except valving gas should be below 500 psi. Valving gas should not go below 200 psi.**
 - a. H₂ Fuel gas supplied by a Whatman hydrogen generator, operating at 40 psi
 - b. N₂ Carrier/Purge gas set at 90 psi
 - c. He Valving gs set at 60 psi
 - d. House air set at 75 psi
 - e. LN₂ Headspace for system blank (steam #1) and for system cryogenics

2. Check the Varian 3600CX GC Instrument

- a. Position the toggle switches to: Normal operations (vs. Canister test)
MFC (vs. Fixed Volume Loop)
- b. Check the pneumatics:
 - Check flow rates: N₂ Carrier gas 20.0 cc/min
 - H₂ Fuel gas check water level and operating psi
 - Air Make-up gas 303 cc/min
 - All needle valves are on
 - Flame for FID is on
- c. Check delay relay switches: valve 1A set to mode "D" (1 second)
- d. Check the setup for PE Nelson 900 Interface box (Interface 1)
- e. Check the setting and readout on the Flow Meter (set at 50 cc/min, channel 2)

3. Check the setup in the Varian Star Workstation

- a. Start Programs / Varian Star 4.5/ System Control
- b. System control configuration: Instrument 1 TPDFID---ADCB(16), 3600(17)
- c. Wait until both ADCB(16) and 3600(17) are online (both icons turn "white" when communication is complete), double click on 3600(17).
- d. Check the status of Instrument 1 by clicking Windows (active SEQ, MTH, SMP)
 - Proceed to Automation menu and select "Stop"

4. Edit pdfid74.mth, pdfid16.smp, and pdfid16.seq

- a. Edit pdfid74.mth:
 - Select File/Method File
 - Open pdfid74.mth
 - Open ADC Board Module16
 - Go to Detector Information
 - Update data filename: MMMDD (i.e., JUN10 for JUNE 10)
 - Save to update detector information
 - Exit, Save again
- b. Edit pdfid16.smp:
 - Select File/SampleList File
 - Open pdfid16.smp
 - Select 8134SSV (Stream Selector Valve), "OK"
 - Update the previous samplelist with the new information
 - Check the 5 step relay event:

<u>Time (min.)</u>	<u>Relay 1</u>	<u>2</u>	<u>3</u>	<u>4</u>
--------------------	----------------	----------	----------	----------

0.00	-	-	-	-
0.01	1	-	-	-
1.00	1	-	3	-
7.00	-	-	3	-
7.20	-	-	-	-

- Print out the sample list by selecting "File" and "Print"
- Check the sample list, including the number of injections, and the streams on the printout
- Make necessary corrections in the pdfid16.smp
- Save pdfid16.smp and close the samplelist window

c. Edit pdfid16.seq:

- Select File/Sequence File
- Open (not activate) pdfid16.seq
- Edit sequence C:\Star\pdfid74.mth C:\Star\pdfid16.smp
- C:\Star\pdfid\ldle16.mth C:\Star\ldle16.smp
- Under File, Save as pdfid16.seq

5. Edit Turbochrom 4.1 Data System Information

- a. Start Programs/Tc4/TCNav, press "Continue".
- b. At this moment, only PDFID16 is configured
- c. Click on "Build Sequence" button
 - i) Select File
 - ii) Open a default or an old sequence
 - iii) Save the selected sequence with the current name (e.g. OC01T sequence stands for the sequence created for October 1)
 - iv) Edit Channel A (Channel B is not used)
 - v) Change file information to current analysis date by selecting Change/Rename Files
 - Enter starting and ending rows (starting cycle number should match starting row)
 - Enter current Base File Name (e.g. OC01 stands for October 1)
 - Check directory C:\TC4\DATA16
 - Check channel A, and all three boxes for raw files, result files, and modified raw files (modified raw files are not used for this analysis)
 - Check "OK", and Save.
 - vi) Print sequence, and check for accuracy
- d. Click on "Analysis Setup" button, and check the following parameters:
 - i) Select "Sequence" in the Setup box
 - Instrument PDFID16
 - Sequence C:\TC4\DATA16\OCT01T.SEQ for the current sequence
 - Data Path C:\TC4\DATA16
 - ii) Select starting and ending rows

- iii) Enter operator's initials
- iv) Interface Data Buffering: Multiple runs
- v) Ensure that Suppress Processing is checked, click "OK" to download the sequence
- vi) The mouse pointer will change into an hourglass indicating the sequence being downloaded
- vii) Click on "Real Time Plot" button to check that the sequence has been properly downloaded, and to view real time events

6. Start the Varian GC

- a. Check to make sure that the flame for the FID is on
- b. Go to the Varian Star Workstation
- c. Go to File/SequenceFile, Activate pdfid16.seq, and select "Begin"
- d. Wait for the GC response to the information that has been downloaded
- e. Press "reset" on GC if the instrument fails to respond
- f. Listen for cryogenics valve to open